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Supercritical CO_2 based Green Technologies for the Consolidation of Foams in Cultural Heritage

The Case Study of Robert Enke's Pair of Gloves

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Dissertation presented at Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, in fulfilment of the requirements for the Master's degree in Conservation and Restoration

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Abstract

The presence of plastics bearing a testimony of the modern and contemporary society has significantly increased in museum collections over the last decades. The preservation of some polymeric materials, namely foams, can be a highly demanding challenge for conservators due to inherent characteristics such as ephemerality and irreversible ageing in short time. The pair of goalkeeper gloves belonging to Robert Enke (*Museu Benfica – Cosme Damião*) is an example of a foam-based object showing a severe condition only after a few decades. Made of a polyisoprene, polybutadiene and polystyrene based foam, the cohesion and mechanical resistance of the gloves are severely endangered and so far, no efficient and safe treatment methodologies have been found for these cases. Based on a significance assessment, it was concluded that the authenticity of the object was intimately related with its materiality and that a consolidation treatment was of the utmost importance to preserve it. Therefore, in this work, conservation efforts were directed to the preservation of this highly degraded foam by studying the potential of a novel methodology for its consolidation based on supercritical carbon dioxide ($scCO_2$).

Despite the successful application of $scCO_2$ in a wide range of conservation treatments for different materials, its application in the preservation of foams is still an unexplored field. Considering the unique and versatile features of supercritical fluids (such as a highly tuneable solvent behaviour, low viscosity, high diffusion rate and lack of interfacial tension), it is expected that $scCO_2$ can be applied as a carrier for consolidants, allowing an in-depth and homogeneous impregnation with minimal interaction.

This work presents a preliminary study regarding the safety and efficacy of a consolidation with $scCO_2$ as a carrier to treat this composite polymeric foam. Several consolidants were tested in foam samples at different test conditions. Visual, physical and molecular alterations were followed by pre and post-treatment characterizations, which included macro and microscopic analyses, dimension and mass variation measurements, colourimetry and infrared and Raman spectroscopies. Results suggest a successful impregnation of poly(vinyl acetate) at 40°C and 280 bar. Although further research is still needed to confirm the safety and efficacy of the method, the promising results show this technology as a potential alternative for the preservation of plastics within cultural heritage.

Keywords: supercritical carbon dioxide; consolidation; foams; polyisoprene; polybutadiene; polystyrene; conservation; cultural heritage.

Resumo

Nas últimas décadas, a presença de plásticos relevantes para as sociedades moderna e contemporânea tem vindo a aumentar significativamente nas colecções museológicas. A preservação de alguns materiais poliméricos, particularmente espumas, pode ser um desafio exigente para os conservadores devido a características inerentes como efemeridade e irreversibilidade da sua degradação num curto prazo. O par de luvas de guarda-redes pertencente a Robert Enke (Museu Benfica – Cosme Damião) é um exemplo de um objecto constituído por uma espuma à base de poliisopreno, polibutadieno e poliestireno, a qual apresenta uma condição severa após somente algumas décadas. A coesão e resistência mecânica das luvas estão severamente em risco e, até agora, nenhuma metodologia de tratamento segura e eficaz foi encontrada para estes casos. Com base na avaliação da sua significação cultural, concluiu-se que a autenticidade do objecto se encontra intimamente relacionada com a sua materialidade, sendo crucial um tratamento de consolidação para a preservar. Assim, neste trabalho, os esforços de conservação focaram-se na preservação desta espuma altamente degradada através do estudo do potencial de uma metodologia inovadora para a sua consolidação com dióxido de carbono supercrítico ($scCO_2$).

Apesar do êxito da aplicação do $scCO_2$ em vários tipos de tratamentos de conservação de diferentes materiais, a sua aplicação na preservação de espumas é ainda uma área inexplorada. Considerando as características únicas e versáteis dos fluidos supercríticos (tais como um comportamento solvente altamente manipulável, baixa viscosidade, alta taxa de difusão e inexistência de tensão superficial), é expectável que o $scCO_2$ possa ser aplicado enquanto solvente para consolidantes, possibilitando uma impregnação em profundidade e homogénea com interacção mínima.

O presente trabalho é um estudo preliminar sobre a segurança e eficácia de uma consolidação com $scCO_2$ para o tratamento desta espuma polimérica compósita. Este envolveu ensaios com vários consolidantes em espumas modelo, tendo sido testados vários parâmetros de utilização. Alterações do foro visual, físico e molecular foram seguidas através de caracterizações pré e pós tratamento, as quais incluíram análises macro e microscópica, medição das variações dimensional e gravimétrica, colorimetria e espectroscopias de infravermelho e Raman. Os resultados sugerem o êxito da impregnação com poli(acetato de vinilo) a 40°C e 280 bar. Apesar de ainda ser necessário um estudo mais aprofundado para a confirmação da segurança e eficácia do método, os resultados promissores mostram esta tecnologia como uma potencial alternativa para a preservação de plásticos do património cultural.

Palavras-chave: dióxido de carbono supercrítico; consolidação; espumas; poliisopreno; polibutadieno; poliestireno; conservação; património cultural.

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Symbols and Notations

Å	ångström
δ	Bending vibration
Δ	Variation
Δ*E**	Total colour variation
μ	Micro
ν	Stretching vibration
$_{as}$	Antisymmetric vibration
ATR	Attenuated Total Reflectance
cm	centimetre(s)
CO_2	Carbon Dioxide
CP	Critical Point
FTIR	Fourier Transformed Infrared Spectroscopy
g	gram(s)
IR	Infrared
m	Medium
mm	millimetre
M_w	Weight average molecular weight
OM	Optical Microscopy
p	Pressure
p_c	Critical Pressure
PB	Polybutadiene
PB72	Paraloid^{TM} B72
PI	Polyisoprene
PS	Polystyrene
PVAc	Poly(vinyl acetate)
$_{s}$	Symmetric vibration
s	Strong
$scCO_2$	Supercritical Carbon Dioxide
SCF	Supercritical Fluid(s)
T	Temperature
T_c	Critical Temperature
T_g	Glass Transition Temperature
T_m	Melting Temperature
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
vs	Very strong
w	Weak

Chapter 1. Introduction

The present study is integrated in the PlasCO_2 – *Green CO_2 Technologies for the Cleaning of Plastics in Museums and Heritage Collections* research project, coordinated by Professor Joana Lia Ferreira and financially supported by *Fundação para a Ciência e Tecnologia* (PTDC/ARTOUT/29692/2017). The project aims to develop new conservation treatments with liquid and supercritical carbon dioxide to overcome the limited existing options for the preservation of materials belonging to the 20th and 21st century cultural heritage, in particular for foams. Despite its notable advantages and diverse application in a wide range of fields, including several conservation treatments [1-3] (Section 1.2), to our knowledge the application of this technology is still an unexplored field for the treatment of plastics from modern and contemporary heritage, namely cleaning and consolidation.

The present work is a preliminary study of the safety and efficacy of a consolidation treatment with supercritical carbon dioxide for the long-term preservation of degraded foams. The primary purpose was to minimize, and ideally eliminate, the risks and problems associated with traditional application methods, such as brush and facing (which require direct contact and may induce further material losses), or spray and nebulisation (which promote a shallow penetration or uncontrollable homogeneity of application of the consolidant). Considering the versatile characteristics of supercritical carbon dioxide and its tuneable solvent behaviour, expectations were that it might be able to diffuse through the foam and carry a solubilized consolidant, applying it in depth and uniformly with minimal interaction. The motto for this study was a highly degraded foam of a pair of goalkeeper gloves belonging to *Museu Benfica – Cosme Damião* (Figure 1.1 and Figures II.1 and II.2 in Appendix II), possibly composed by a blend of polyisoprene, polybutadiene and polystyrene, as indicated by infrared spectroscopy analysis (Chapter 2). The first approach was the

Figure 1.1 - Back side (A) (© *Museu Benfica - Cosme Damião*) and palm side (B) of Robert Enke's pair of gloves.

contribution to a comprehensive biography and history of the object, through documental research and production of new documentation for an insight on its materiality, degradation, significance and conservation priorities. Model samples were selected and characterized, along with several consolidants, to assess the safety and efficacy of the method as a consolidation treatment in different test conditions. Visual, physical and molecular alterations were followed by pre and post-treatment characterizations, which included macro and microscopic analyses, dimension and mass variation measurements, colourimetry and infrared and Raman spectroscopies (Chapters 3 and 4).

1.1 Plastics in heritage collections: a conservation challenge

Plastics have had a significant and sometimes revolutionary influence in countless aspects of the everyday life [4], especially since the 1960s [5]. These modern materials include a wide range of synthetic polymers with various forms (such as solids, foams, fibres, films, among others) and versatile features and properties, which triumph has reached not only industrial and technological fields, but also art, fashion and design [4, 5]. Reflecting the statement made by artists Marcel Biefer and Beat Zgraggen in 1991 that 'plastic artefacts will be the most important witness to our time' (Biefer & Zgraggen, 1991 as cited in [4]), museums have been acquiring objects bearing testimony of the modern and contemporary societies, and the presence of plastics in heritage collections have significantly increased [4, 6].

From a conservation perspective, degradation of a polymeric material belonging to the cultural heritage can be defined by any change with adverse effects on its physical or chemical properties, function and/or significance, as a result of physical, chemical and/or biological factors (Appendix I) [4]. The resistance of plastics and extent of their chemical degradation can be highly variable [4, 7], and the so-called 'malignant plastics' [1] bear particular inherent characteristics that turn their preservation into a highly demanding challenge. Firstly, the chemical complexity of plastics can contribute to an unpredictable long-term behaviour and ageing [6], as a result of countless different chemical formulations when considering the variety of existing polymers, possible mixtures and additives (including plasticisers, stabilizers, fillers, antioxidants, colourants, among others) [4]. A further challenge is the relative ephemeral nature for the conservation standard and the particular inherent instability of 'malignant plastics' [5, 9]. They are produced with an implicit 'disposability' [5] due to the manufactures' greater concern with short-term physical and mechanical properties of an object over long-term performance [10]. Therefore, degradation of some plastics in museum collections can emerge only within 5 to 35 years of acquisition [4], contrasting with other heritage objects such as stone or paint, which lifetime longevity is expected to outlast us [6]. Ageing processes are dependent on chemical formulation

[1] 'Malignant plastics' in museum collections are the most susceptible plastics to ageing, producing noxious degradation products that may induce damage to other objects in the vicinity. They include a relatively small set of plastic types, namely cellulose nitrate, cellulose acetate, poly(vinyl chloride), polyurethane (especially foams) and rubber (especially highly vulcanized hard natural rubber, such as ebonite and vulcanite) [7, 8].

and overall history of the material, namely the conditions to which they were submitted during production and exposure to degradative agents (such as light and UV radiation, oxygen, heat, moisture, chemicals and pollutants) throughout their lifetime [4, 7] (Appendix I). Ageing can be detectable in plastics by a change in appearance and feel or by an odour release, and unfortunately, these changes are commonly unavoidable, progressive and irreversible [4]. It may also increase the sensibility of some plastics to many common solvents, leading to unpredictable responses to treatments and complicating interventive practices [4, 11, 12].

Elastomeric materials, namely foams such as polyurethane and the material of the gloves in study, are particularly prone to chemical degradation. Their porosity facilitates the access and reaction with degradation agents, such as environmental oxygen and radiation [9, 13], culminating in a process known as photooxidation [13, 14]. Oxidation of a polymer involves the absorption of oxygen from the atmosphere and takes place in reactive bonds and sites such as carbon-carbon unsaturated bonds and tertiary carbons of branched chains. Two main degradation mechanisms compete during this process, the abstraction of a hydrogen in the allylic position (main route for dienic rubber photooxidation) and addition of radicals to unsaturated bonds [14, 16]. A continuous chain reaction is set off until no polymer remains, which can be divided into three main stages - initiation, chain propagation and termination. In the initiation step, when energy is available (for example, from heat or light), hydrogen from the carbon atom in the α-position of double bonds can easily undergo radical attack by electrons from oxygen molecules (abstraction), generating a pair of highly reactive free radicals [14, 17]. Subsequently, several types of oxygenated species are formed when, in the chain propagation step, these products continue to react with oxygen molecules and with the polymer itself (abstraction and addition processes). Consequently, peroxy radicals ($RO^{\bullet}_2$) and hydroperoxides (ROOH) are produced, the latter one decomposing by scission of the oxygen-oxygen bond and producing two more unstable radicals ($RO^{\bullet}$ and $HO^{\bullet}$). Degradation continues by further reaction of these free radicals with oxygen until the terminal step, when radical sites combine and react with each other, forming non-radical species (for oxygen) with carbonyl groups, such as esters (RCOOR), ketones (RCOR) and aldehydes (RCOH) [15, 18, 19]. On the other hand, light induced degradation can also occur when radiation is absorbed by chromophores (light-absorbing groups). These functional groups can be present in the chemical structure of the polymer backbone, in additives, in impurities introduced during manufacture or in molecules or moieties that are formed by oxidation. The most susceptible sites for photochemical reactions are unsaturated carbon double bonds and carbonyls, leading to the formation of free radicals that further react with oxygen [20, 21].

Since both oxygen and some radiation promote the cleavage of specific chemical bonds of polymers and additives, chemical and structural changes are eventually inevitable. Besides the formation of new chemical groups, which can lead to alterations in colour (yellowing), the cyclic photooxidation reactions also lead to the competition between two degradation processes, chain-scission and crosslinking [16]. The former one is the most common and is characterized by the disruption of the polymer chain into several segments, causing a significant reduction of its molecular weight. Physical and mechanically, this change implies loss of strength

and cohesion of the material, leading to cracking and crumbling [4, 16]. A crosslinked structure can simultaneously be formed, via migration and recombination of radicals, leading to the formation of new intermolecular covalent bonds. The resulting three-dimensional network promotes an increase in molecular weight and, subsequently, a decrease in solubility and flexibility of the material [14, 22]. Although competing during degradation, the mechanism that precedes and prevails depends on the chemical composition and properties (such as morphology) of the polymer, exposure time and wavelength of the UV radiation [14- 16].

Besides the inherent characteristics of some plastics described above, it is also important to highlight that the recent presence of these materials in museum collections reflects on a less extensive wealth of knowledge gathered by conservators, when compared to more classical materials, including stone and paints [6]. As a result, adequate conservation treatments are still limited or even lacking for some cases, such as the consolidation of foams [23], which justifies the urgent need of research and development of new strategies to approach the problematic preservation of plastics.

1.2 Supercritical CO_2: properties and applications in the conservation field

In an attempt to develop more sustainable chemical processes, from an environmental, safety and economical point of view, supercritical fluids (SCF) technology have had a recent advance in the last decades [1]. Due to their unique solvent characteristics, SCF have been touted as green alternatives to reduce or totally replace the excessive use of organic solvents in several areas such as extraction, synthesis, fractionation, pharmaceutical formulation, among others [2]. In particular for the polymer industry, new routes of polymerization and polymer processing with SCF have been studied, which include particle formation, purification/extraction, foaming, extrusion, alteration of properties (like viscosity and glass transition temperature, T_g) and impregnations with low molecular weight (M_w) substances [1-3].

As shown in Figure 1.2, a pure component is considered in a supercritical state if its temperature (T) and pressure (p) are above its critical values (critical temperature (T_c) and pressure (p_c)), which define a characteristic critical point (CP). At these conditions, the gas/liquid phase boundary (red line) no longer exists and a homogenous phase of a highly compressed gas (supercritical) is formed, as a result of the converging of the densities of both phases [2, 24]. At a characteristic microscopic level of 10-100 Å, Baldyga [25] defines the supercritical phase as having a variable number of clusters (depending on T and p) of augmented density with a structure similar to liquids, surrounded by less dense and more chaotic regions of compressed gas, leading to high compressibility near the CP. As a result, SCF can be considered as “hybrid solvents” [2] since they can simultaneously combine the physical and chemical properties of liquids and gases. Similarly to a liquid, they have a relatively high density and the ability to dissolve solids and compatible liquids, through the formation of high solvation areas around the solute molecules [3, 26]. As a gas, they also feature low viscosity, high diffusion rate and lack of interfacial tension, penetrating readily in a wide range of materials [2, 26]. Additionally, properties such as density, viscosity and solvent behaviour can be highly tuned from liquid-like

to gas-like without any phase boundary being crossed and, subsequently, a new phase being formed. This versatility is achieved by simply adjusting the conditions (T and p) within the supercritical area, which allows the tuning of a fluid's selectivity and specificity [2, 24].

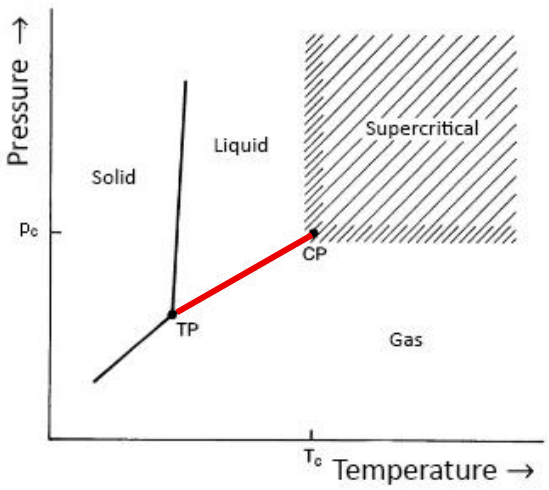

Figure 1.2 - Pressure-temperature phase diagram of a pure component and definition of a supercritical state (adapted from [24]).

Carbon dioxide (CO_2) has been one of the most extensively used SCF in a variety of applications and processes, particularly due to its innocuity, low cost and readily accessible critical point (T_c = 31°C and p_c = 73.8 bar [24]) when compared with other gases [2]. Besides the previously described SCF properties, CO_2 is also an environmentally benign solvent due to its non-toxicity, non-flammability and 'volatility', which facilitates the solvent removal and subsequent recycling and reutilization [2, 3].

Regarding its solvent strength, supercritical CO_2 ($scCO_2$) is considered a feeble SCF solvent with an ambivalent character for its simultaneous low polarity, low polarizability and strong quadrupole moment, the latter one having a dominant role in determining the solubility of a substance [27]. It is considered a reasonable solvent for many non-polar and some polar molecules with low M_w, including most common monomers and oligomers. However, according to the literature, the predominant trend is a decreased solubility in $scCO_2$ with increasing molecular size (translating in a significant increase of the CP), which explains the limited solubility exhibited by larger components and polymers with M_w above 1000 [1, 2, 27]. Considering the chemical composition of the foam in study, different researches confirm most polymers insolubility in CO_2 regardless of T and p, including polystyrene [27] and polyisoprene [28]. However, it is important to highlight that the solubility of CO_2 in many polymers may be substantial, i.e. the diffusion and sorption of the gas that results in the material's swelling. This phenomenon can be intentionally used for impregnations and extractions of low M_w substances by CO_2 and for manipulation of the polymers' properties, namely reduction of T_g (plasticization effect, due to an increased chain mobility) and melting temperature (T_m) [2, 29]. On the other hand, as a result of several complex chemical characteristics and interactions, some polymers exceptionally exhibit solubility in CO_2, such as fluoropolymers (or at least partially fluorinated), poly(methyl acrylate) and poly(vinyl acetate) [27, 28, 30]. The chemical architecture of these polymers demonstrates a significant impact in increasing solubility, particularly a flexible backbone (low T_g) and high free volume, since stiffer chain segments are more difficult to dissolve. Polymers with weak interactions between their segments and with an interaction site such as a carbonyl group, are also more prone to interact and solubilize in CO_2. Solubility of poly(vinyl acetate), even with a high molecular weight, is described as a consequence of the easy access of CO_2 to the carbonyl groups of the polymer [27]. Additionally, the temperature and pressure tuneability allows the manipulation of

the dominant interchange energy in operation, i.e. intermolecular forces between polymer-polymer, polymer-CO_2 and CO_2-CO_2 [27, 28, 30].

The application of the unique and versatile characteristics of CO_2 has also become enticing for the preservation of the cultural heritage, and it has been tested and applied in several materials and for different treatment purposes. Ricardo *et al*. [3] presented a review on the most significant studies on the conservation treatment of several heritage materials with liquid and supercritical CO_2, including paper deacidification, textile cleaning, waterlogged wood drying and extraction of stone protectives and pesticides from ethnographic objects. To the present date, several other researches have corroborated the successful results of these treatments in new case-studies or have tested new treatments with CO_2 in the conservation and archaeological fields. They include paper deacidification [31-33] and disinfection of fungi [34], textile cleaning [35, 36] and disinfection [36] and decontamination of ethnographic materials, such as wooden artefacts [37, 38], leather [38, 39] and textiles [38]. Moreover, drying of cork [40] and osteological remains [41], hydration of dry wood [42] and extraction of organic matter form ceramics [43] and archaeological artefacts (burial and embalmment materials) [44] have also been studied. Hénon *et al*. [45] also studied the solubility of several perfluoropolyethers (frequently used as stone protectives) in CO_2, demonstrating the viability of the method to substitute toxic solvents and to reverse previous treatments. However, to our knowledge, there are no studies on the application of CO_2 for the treatment (namely cleaning and consolidation) of any synthetic polymer material, including polymeric foams in modern and contemporary cultural heritage objects. Thus, this study is the first research regarding this topic, attempting to contribute to the fulfilment of a lack of knowledge concerning the conservation of polymeric foams in cultural heritage, which urgently lack for effective and safe consolidation methods.

Chapter 2. Case-study: Robert Enke's goalkeeper gloves

As previously mentioned, the pair of goalkeeper gloves belonging to the football player Robert Enke (Figure 1.1 and Figures II.1 and II.2 in Appendix II) was the motto for the present research. It is currently held by the *Museu Benfica – Cosme Damião*, after its donation in 2016 by the well-known supporter Guilherme Cabral. The donation was particularly motivated by the inexistence of another item in the museum belonging to Robert Enke and by the physical condition of the pair of gloves, which requires proper conservation and storage. Furthermore, the palms of both gloves are signed by the player and have an inscription dedicated to Guilherme Cabral, which features were considered to highly contribute to the value of the object (Section 2.2.1). Although there are no physical evidences of the brand of the gloves, the Documentation and

Information Centre of *Museu Benfica* states that Reusch was the brand most frequently used by the player. In the present study, it was possible to corroborate this information with the Reusch's Department of Product and Design. Confirmation of the brand was based on several features of the gloves' design, particularly the presence of triangles at the middle, ring and little fingers, the use of a silver like base material on the back side, the additional latex patch on the strap on the palm side and the name on the strap itself. A detailed technical sheet of the object is presented in Appendix II.

The present study focuses on the condition assessment and material characterization of the highly degraded foam covering both palms of the pair of gloves (Section 2.1) as its degradation is endangering the physical stability and value of the object. Based on a significance assessment, different conservation strategies were considered to treat the foam, including a novel consolidation approach with $scCO_2$ (Section 2.2).

2.1 Material condition and characterization

The condition of the foam was classified as unacceptable[2], due to its high level of deterioration and instability, active degradation process, loss of function and need of an immediate treatment to restore its stability and to allow a safe handling of the object (e.g., for future interventions or exhibition). Some of the observed damages include an intense yellowing, physical deformations and superficial material losses. Structural damages shown in Figure 2.1 such as a severe cracking and fracturing, fragments in risk of detachment or already lost (lacunae) are compromising the physical stability of the material, as well as the inscriptions and signatures. Other observed damages include material deposit by transfer and occurrence of dark and brown stains. A detailed description and mapping of the damages are presented in Appendix III.

A preliminary characterization based on infrared microspectroscopy (μ-FTIR) was performed elsewhere [46] to assess the chemical composition of the foam. The obtained information was complemented by a patent research on sports equipment, namely goalkeeper gloves, and shock-absorbing materials [47-51].

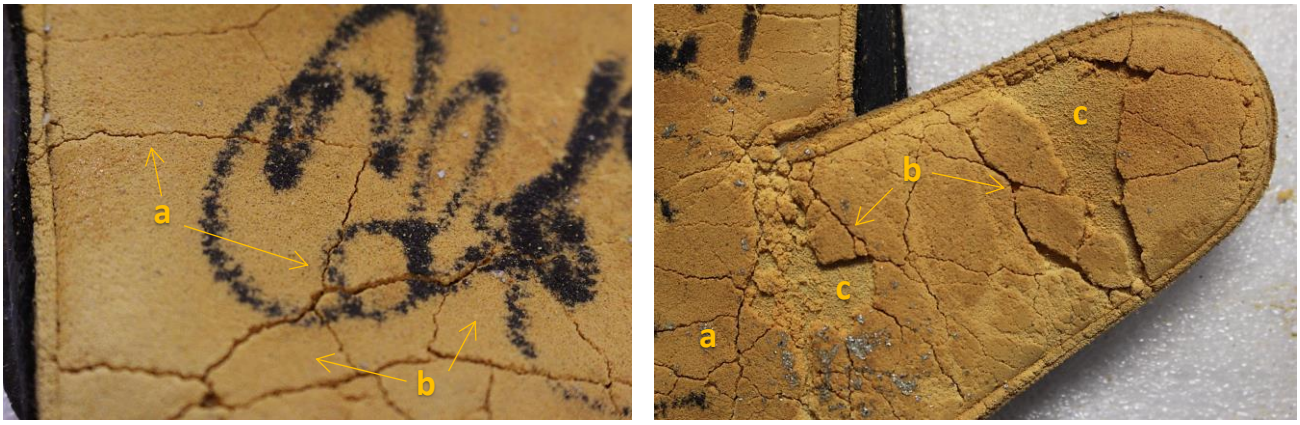

Figure 2.1 - Details of the gloves foam showing different types of degradation, namely yellowing, cracks and fractures (a), several fragments in risk of detachment (b) and lacunae (c).

[2] The highest level according to the four-category system proposed by Keene [55] to classify the degradation of an object.

It was concluded that the material is probably a synthetic latex[3] based polymer, specifically a blend of polyisoprene (PI), polybutadiene (PB) and polystyrene (PS) (chemical structures in Appendix IV), with the last two possibly as a copolymer.

Infrared analysis of the gloves foam is presented in Figure 2.2, along with a comparison with PI and poly(butadiene-styrene) references, which allowed the assignment of some absorption bands to these polymers. According to the photodegradation study by Santos *et al.* [15], the absorption bands at 2966, 2933, 2875, 1450 and 1377 cm^{-1} are attributed to PI, which tend to persist even after the exposure of the polymer to UV radiation. Despite the overlap of some characteristic bands of PI and PB (namely at 2916 cm^{-1} and 1450 cm^{-1} observed in the references' spectra) due to their chemical structure similarity (Appendix IV), the absorption bands at 964, 910 and 702 cm^{-1} are attributed to PB and provide useful information about its isomers. Corresponding to C-H bending vibrations of *trans*-1,4, 1,2 and *cis*-1,4 units respectively [22, 54], the presence of absorption bands in the gloves foam at 914 and 701 cm^{-1} not only may confirm the presence of butadiene, but may also suggest a higher percentage of 1,2 and *cis*-1,4 isomers. PS presence is mainly identified by the absorption bands at 762 cm^{-1} and 701 cm^{-1}, the later one attributed to an overlap of deformations of its aromatic rings with the C-H bending vibrations of *cis*-1,4-butadiene [17, 54].

As discussed in the Introduction, elastomeric materials, especially those derived from dienes, are particularly susceptible to photooxidation and the gloves foam is no exception. The most vulnerable sites to oxygen and photon attack are the many double carbon bonds that compose the material [14, 15, 56]. Photooxidation processes lead to chemical alterations that are reflected on several changes in the infrared

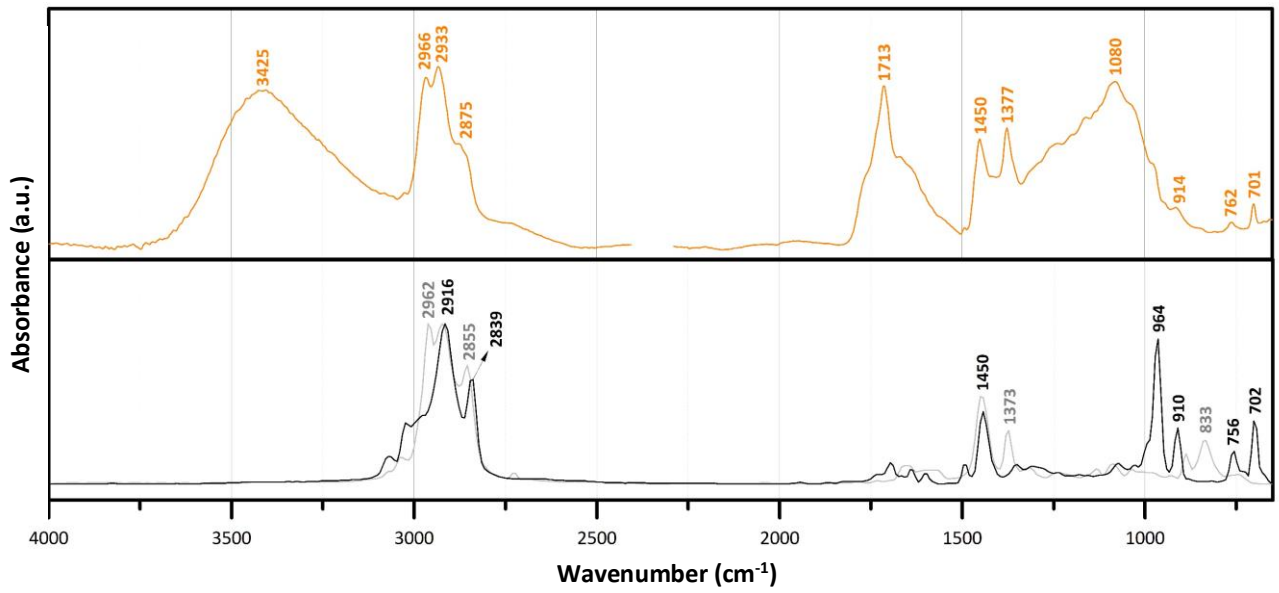

Figure 2.2 - Infrared spectra of the foam from Robert Enke's gloves (orange), comparing to 1,4-*cis* polyisoprene (grey) and poly(butadiene-styrene) (black) references.

[3] According to the literature, latex is a polymer emulsion or sol, i.e. a dispersion in water of small colloidal particles containing several macromolecules. It is stabilized by the presence of emulsifiers and isolation of the polymer can be achieved by the addition of ionic substances, leading to coagulation. Polymer lattices can be produced synthetically by emulsion polymerization, or occur naturally, as it is the case of natural rubber [52, 53].

spectrum of a material. Spectral changes in the gloves foam observed in Figure 2.2, when compared to the spectra of polymer references, are in agreement with the degradation pattern of these polymers described in the literature. The most affected vibrational modes are those related to unsaturated bonds, such as C=C stretching and =C-H wagging at 1670-1650 and 850-800 cm^{-1} respectively, overlapped with the appearance of new features [15, 22]. Chain scission, as one of the consequences of ageing processes, also results in a decrease of the C-H stretching bands between c. 3000-2750 cm^{-1}. The development of new absorption bands at 3400 cm^{-1} can be assigned to stretching vibrations of hydroxyl functional groups, suggesting the presence of alcohols and carboxylic acids [15, 16, 22]. The new carbonyl stretching band at 1700 cm^{-1} is characteristic of esters, ketones and aldehydes (the observed shoulder at higher wavenumbers is assigned to the presence of anhydrides, lactones and peracids) [15, 17]. Formation of hydroperoxides, esters and ethers species also lead to an increase of C-O-C and C-O-O stretching vibrations between 1250-1080 cm^{-1}.

The incorporation of humidity and salts from sweat in the foam is also suggested as an additional degradation agent for the case-study. As it will be further explained in the Experimental section (Chapter 3), this hypothesis was corroborated by the ageing experiments performed in test gloves, in which a combination of UV-Vis light exposure and relative humidity cycles had the most similar degradation pattern to the case-study. Furthermore, the mechanical wear (which induced stress into the material) prior to its deposition into the museum collection, along with inappropriate storage conditions up to the entrance in the museum storage, may have also influenced its degradation.

2.2 Discussing conservation approaches for Robert Enke's gloves

2.2.1. Significance assessment: meaning and values

Conservation decisions can influence, with a variable impact, the construction of the societal memory of a cultural object or collection [57], meaning how it is perceived and transmitted to present and future generations. Thus, the decision-making process for their preservation must be carefully undertaken, especially when considering that authenticity may or may not be found exclusively in the original materiality [9]. Thus, the assessment of the heritage significance is a vital step to preserve their identity and values in the long-term and should not aim for the physical conservation of the materials for their own sake, but also, and more important, for the preservation of the values embodied by them [58]. Although being a topic widely studied, defining the significance of an object or collection is complex and highly subjective. Due to the systematic approaches already conducted by Avrami [58] and by Russell, in the publication *Significance 2.0* [57], these were the main references selected for the evaluation of the meaning and values of the gloves in study.

According to Russell *et al*., 'significance defines the meanings and values of an item or collection for people and communities through research and analysis, and by assessment against a standard set of criteria [57]. However, different values may be considered for the same object since significance is not an

absolute state nor an objective and inherent feature, but rather depends upon the constant mutation of the context in which the object is inserted and the perspective of who is assessing it. A significance statement is then a temporary and contextual perception that defines the key values that express how, why and to whom the object is relevant in a given moment in time [9, 57, 58]. Through the exploration of all tangible and intangible elements that contribute to the meaning and value of an object, and the identification of the community that recognizes this set of criteria (stakeholders), a comprehensive identity of an object can be achieved [57]. This procedure should be part of the decision-making process for the development, care and management of the cultural heritage, in order to make good and informed decisions when establishing personalised conservation plans [57]. The identification and ordering of the values clarify conservation priorities and, according to Avrami, 'serve as a vehicle to inform decisions about how best to preserve these values in the physical conservation of the object or place' [58]. Since ethical dilemmas may arise during the decision-making process of more complex case-studies, this approach can also help when the final decision leads to conservation compromises.

As previously discussed, the foam of the pair of gloves in study is characterized by its ephemeral nature, which launches highly demanding conservation challenges. The assessment of the significance of the pair of gloves was crucial to understand its values and identity and to establish a conservation plan to preserve it. This assessment was undertaken by determining the stakeholders and exploring all features which contribute to its meaning, based on provenance, context, history, memories and stakeholders. To answer the question *To whom are these gloves significant?*, three stakeholders were identified: the institution *Sport Lisboa e Benfica*, its football community and the previous and current owners. The pair of gloves is relevant to the current owner, *Museu Benfica - Cosme Damião*, which represents the interests of the conservators and of other experts who care for its preservation, i.e. the object not only represents a piece of the history of Benfica, but is also the only one held by the institution that as actually belonged to Robert Enke. As the football sports club Benfica holds a stronger economic interest than the museum, it was considered a different stakeholder. Additionally, it was also included the previous owner, Guilherme Cabral, a well-known supporter of Benfica who donated the pair of gloves and to whom the inscriptions are dedicated to, along with Benfica's community, meaning all the supporters that acknowledge the contribution of Robert Enke to the history of the institution and recognize the piece of memory represented by this object in the collection.

Meanings and values embodied in the gloves were found to be often interconnected, which have complexified their definition process, even though some features revealed to be unifying links for all the determined values. Part of the recognized meaning of the object is held by its provenance, since the donation by Guilherme Cabral can be understood as a donation to all other supporters, reaching not only Benfica's supporters, but everyone with a memory of Robert Enke. All values are also found to be intrinsically related to the context in which the object is inserted, since Benfica is an aggregating link between Robert Enke, the gloves and its stakeholders. Moreover, it is in *Museu Benfica* that the connection between the memory of the

player and the community that recognizes his value (and consequently the gloves significance) subsists, suggesting a strong emotional value. Also, contributing to this value is the presence of signatures and inscriptions, which are considered to inspire an emotional attachment from the entire community and not solely from Guilherme Cabral. On the other hand, the pair of gloves holds other elements that grant it an autobiographic character. They include the identification of the player on the wrist and the features related to mechanical wear (and subsequent degradation patterns, particularly cracks and lacunae on the fingertips, finger joints and palms), through which it is perceptible the impact of the ball and the mechanics of the hands themselves. The weight of time physically represented by these features evokes the memory of the player and allows one to be transported to that period, imagining how and when the gloves were used. The appearance of the object is then representative of its history, turning it into an autobiographic and a memorial item with strong historical and aesthetic values. Values of unicity and rarity are also identified since, as previously mentioned, it is a unique object in the collection and, as a pair of gloves signed by Robert Enke, it is also a rare item. It is also important to highlight the potential scientific and research values, since the object can be used as a case-study to undertake research in other fields, such as degradation, innovative conservation treatments, history of technology or history of sports equipment.

Concluding, the authenticity of the gloves is considered to be intimately related with its materiality and aesthetic appearance. It is identified in physical and autobiographic features, especially the signatures, inscriptions and tangible representation of its use and passage of time (such as the cracks and lacunae). Due to its ephemeral nature and advanced chemical degradation, the main conservation challenge will be to find a balance between the urge to chemical and physically stabilize the foam while, simultaneously, preserve the intangible and tangible aspects (autobiographic features) that embody its identity.

2.2.2. Conservation options for the preservation of the identity of Robert Enke's gloves

Several conservation approaches could have been considered for the preservation of the materiality of the gloves including the application of a stabilization and consolidation treatment, production of a replica and assumption of its degradation [5, 9]. The latter one was discarded for undoubtably compromising the physicality and, subsequently, the values and meaning of the object, eventually leading to its complete loss. On the other hand, replication is a controversial conservation strategy that can be considered for objects with distinct values, as it was discussed already in 2007 in the colloquium 'Inherent Vice: The Replica and Its Implications in Modern Sculpture' held at Tate Modern. It was also rejected as a conservation option for this case since the preservation of the materiality that holds the current aesthetic of the gloves is the main conservation priority and cannot be replaced. Consolidation treatments are viable solutions for objects in advanced state of degradation, with a physical structure highly damaged due to crumbling [23]. As the consolidant needs to be applied to the entire surface of a material that is losing its cohesion [23], this treatment might be considered a drastic option for an object as chemical, physical and optical interactions

between the consolidant and the substrate are inevitable, even though required [59]. The decision to undertake a consolidation must also admit its irreversibility, since reversibility would be incoherent with the treatment's own goals and would likely induce further material losses, jeopardising the integrity of the object [60]. However, if future re-treatability is possible [60], it can be a viable option for some materials that are no longer able to maintain their cohesion and are in imminent risk of total loss, such as the case-study. For this reason, stabilization and consolidation treatments were considered a priority to return the physical cohesion and long-term stability and integrity to the material, by discontinuing the active crumbling process and minimizing future material losses. Although a consolidation requires an in-depth impregnation of a consolidant within the substrate [60], it was considered that a compromise towards the originality of the material was necessary to preserve its materiality.

For the success of a consolidation treatment, the substrate must be inherently porous and permeable to allow the impregnation of the consolidant [60]. Moreover, due to chemical alterations, the degradation level of the substrate may compromise the compatibility with a consolidant that is expected to be compatible with the unaged material. Consolidants consist of polymeric products that can have different properties depending on their chemical nature. A set of criteria should be considered when choosing a consolidant, regardless of the material to be treated. It should be nontoxic in the long-term for the substrate and materials nearby, users and environment [10]. The properties and characteristics of the consolidant and its ageing behaviour should be well known to guarantee its physical and chemical stability and compatibility with the substrate in the long-term. These properties include chemical composition, pH, colour, glass transition temperature (which influences the quantity of captured particles at room temperature), flexibility and adhesion strength when cured (to avoid inducing mechanical stress to the substrate), among others [10, 59-61]. Commercial formulations should be avoided for any conservation treatment, since most products are designed considering properties important for industrial purposes that conflict with the conservation standards, such as short-term durability and unpredictable ageing behaviour due to complex formulations. Furthermore, the composition of a product may be altered by manufactures without the users' knowledge, invalidating any studies on its application and long-term properties [10]. Also relevant is the solubility of the consolidant since the compatibility of the solvent with the substrate must be guaranteed. Moreover, the selected solvent will influence the handling properties of the consolidant, enabling the manipulation of its drying time and viscosity, which influences its penetration [10, 59, 61]. Selection of the most suitable application technique must be safe for the condition of the substrate (to avoid further material losses) and should allow an in-depth and uniform application of the consolidant to reduce stress at interfaces [59].

However, it is a highly demanding task to find a consolidation treatment that fills all the ideal conservation requirements and is suitable for the material to be treated, particularly considering its identity, characteristics and future expectations for handling and exhibition purposes. Ethical dilemmas may arise

during the decision-making process, leading to the compromising of some consolidation requirements to satisfy the most important ones for the object [60, 61].

Previously to the present work, consolidation experiments were performed for the treatment of the gloves foam. Several consolidants (Latex Milk 77200 [4], Evacon-R™ [5] and Mowilith® LDM 7667 [6]) and one light stabilizer (Tinuvin® B 75 [7]) were applied in test samples through nebulisation and facing techniques. The details of these experiments are summarized in Appendix V.1. It was concluded that the consolidants applied through nebulisation did not improve the cohesion of the foam, contrary to Mowilith LDM 7667 and Evacon-R™ applied through facing, which had good results when compared to the reference samples. However, facing technique induced further material loss of the fragile foam and did not guarantee a homogeneous and in-depth penetration of the consolidant, compromising the efficacy of the treatment.

2.2.3. Conservation Strategy with Supercritical CO_2

A novel conservation strategy was considered for the consolidation of the gloves in an attempt to overcome the safety and efficacy issues of nebulisation and facing methods, specifically the shallow and inhomogeneous penetration of the consolidant and the invasiveness of the facing treatment. This approach is based on the application of supercritical carbon dioxide ($scCO_2$) as a solvent for consolidants. Due to the characteristics of supercritical fluids, it is expected that this method brings several advantages regarding traditional application techniques. As discussed in the Introduction, they have already been applied for conducting impregnations with low molecular weight (M_w) substances [1, 2]. Their highly tuneable solvent behaviour (by manipulation of T and p) allows the tuning of their selectivity and specificity as a solvent. Additionally, they feature a high diffusion rate and lack of interfacial tension, which enables an easy penetration in a wide range of materials [2, 26]. For these reasons, these features are expected to allow an in-depth transport and uniform application of a consolidant with a minimal, or even inexistent, interaction with the substrate, helping to prevent further losses and contributing to a safer and more efficient treatment. Moreover, it is considered a green technology comparing with most traditional consolidation methods that resort organic solvents, thus being a viable and safer alternative that can be recycled and reutilized [2, 3].

As previously discussed, it is not expected that large molecules and polymers with average molecular weights above 1000 to be soluble in CO_2 [1, 2, 27]. Regarding the polymers of the gloves foam, studies specifically confirm the insolubility of polystyrene [27] and polyisoprene [28]. However, it is important to highlight that these studies were conducted in unaged polymers and their solubility behaviour may alter with degradation, particularly considering that the presence of an interaction site such as a carbonyl group (which

[4] Natural rubber latex.
[5] Non-plasticized aqueous copolymer dispersion based on vinyl acetate and ethylene.
[6] Non-plasticized aqueous copolymer dispersion based on (meth)acrylic acid esters and styrene.
[7] Blend of 20% Irganox® 1135, 40% Tinuvin® 571 and 40% Tinuvin® 765.

is present in degradation products) improves the solubility in CO_2 [2]. Even though solubility in CO_2 may not occur, the sorption of the gas by the polymers may be substantial, leading to swelling and alterations in their mechanical and physical properties, such as reduction of T_g (plasticization effect, as a result of an increased chain mobility) [2, 29]. Although these may be intentional and desirable effects in the polymer industry, from the conservation point of view they may lead to an unpredictable behaviour by the polymers and to irreversible damage in the object, as a result of volume alterations due to swelling. On the other hand, CO_2 sorption by a polymer is also necessary for the success of extraction and impregnation treatments, such as cleaning and consolidations respectively. As a result, the performance of a successful consolidation treatment must be balanced with the preservation of the gloves integrity. Few studies were found regarding the solubility and sorption of CO_2 by the polymers that compose the gloves foam. The tendency for an increase in the solubility and sorption of CO_2 with pressure and decrease in temperature (due to the subsequent increase in the density of the gas) was verified for polystyrene [62-64], polyisoprene and styrene-isoprene copolymers [64]. For the latter one, it was also verified a significant increase in the copolymers' swelling with the increase in isoprene content [64]. However, regarding polyisoprene, another study reported an unexpected increase in the volume of the polymer with temperature, possibly as a result of its cubic expansion [65]. Webb & Teja [66] reported the lack of solubility of CO_2 in a porous and crosslinked polystyrene.

Considering this information, CO_2 is then not expected to solubilize the foam of the gloves, but the gas sorption by the polymer may be possible, which is essential for the impregnation of a consolidant. However, in case of occurrence, swelling must be minimized for the preservation of the integrity of the object. The extent of the swelling cannot be predicted, particularly due to the scarce knowledge about the chemical formulation of the foam (percentage of the polymers and additives) and due to its level of degradation. The priority of the present study must be the safety assessment of the method for the material and its efficacy assessment as a vehicle for a consolidation treatment. For that, visual, physical and chemical characterization before and after experiments were carried out. Safety evaluation should include possible irreversible damages due to CO_2 interaction, such as solubility of the material, swelling and alterations in mass, colour and chemical composition. Efficacy of the treatment should be assessed through molecular analysis along with evaluation of the penetrability of the consolidant and uniformity of its application, as well as the gain in cohesiveness.

Chapter 3. Experimental design

3.1. Materials selection

3.1.1 Foam test samples

Three gloves' foams from different commercial brands (Reusch, Nike and Kipsta; see Appendix V.2) were characterized for selection of appropriate test materials and also for understanding the chemical variability of the material between brands. Excepting for Reusch gloves, which had been previously used in a sports context, all pairs were acquired new and one glove from each pair was then submitted to an artificial ageing[8] for visual and analytical comparison of degradation patterns with the case study. Unaged foams were characterized by Raman spectroscopy and infrared spectroscopy in attenuated total reflection (ATR-FTIR), in which the presence of isoprene, butadiene and styrene were identified, similarly to the case-study. Raman analysis (Figures 3.1) suggests that Reusch foam has a higher content in isoprene (due to the higher intensity of the bands at 1666 and 2913 cm^{-1} [67]), and that Kipsta foam has a formulation richer in butadiene (1003 and 1308 cm^{-1} [69]) and styrene (620 and 1032 cm^{-1} [70]).

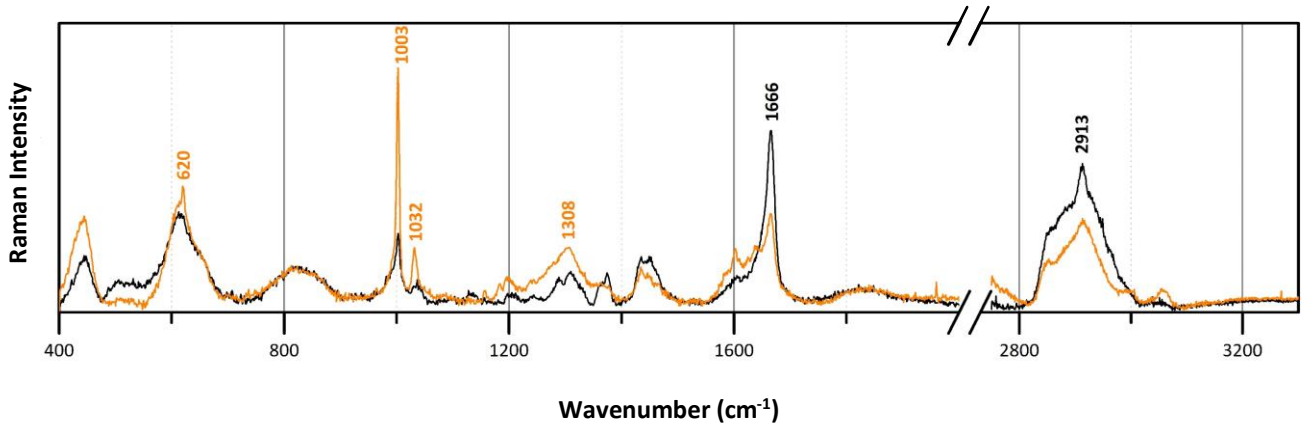

Figure 3.1 – Raman spectra of Reusch (black) and Kipsta gloves (orange), before artificial ageing.

Infrared characterization (Figure 3.2) is in agreement with this analysis, particularly due to the stronger absorption band at 699 cm^{-1} for Nike and Kipsta foams, attributed to a characteristic vibration of styrene. These results indicate a similar chemical composition between brands with different proportions and corroborate the conclusions from the characterization of the case-study (Section 2.1). The spectral changes (band shifts, relative intensities variations and the appearance of new absorption bands) detected in the infrared spectrum of Reusch foam before artificial ageing were attributed to degradation processes, since these gloves were previously used and thus more directly exposed to degradation factors such as radiation,

[8] To simulate the degradation conditions of the case-study, namely exposure to oxygen, UV radiation and humidity (from sweat), the test gloves were firstly aged in a SolarBox, followed by exposure to humidity cycles in an oven.

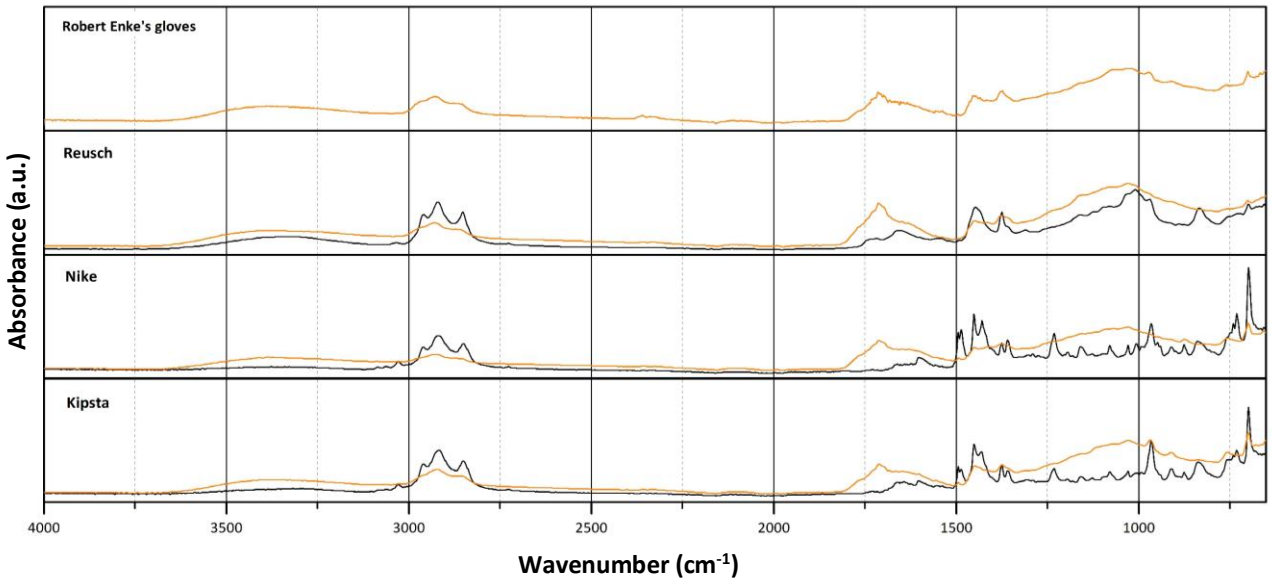

Figure 3.2 – Infrared spectra of the degraded foam from Robert Enke's gloves (orange, top) and comparison with the foams from Reusch, Nike and Kipsta test gloves, before (black) and after (orange) artificial ageing.

humidity, sweat and use (mechanical wear). Aged foams were characterized by ATR-FTIR spectroscopy[9] (Figure 3.2). Apparently, all foams show similar degradation patterns between them and the case-study, suggesting that the verified variations in the polymers' content may not significantly affect their degradation path under the tested ageing conditions.

The foams from the selected commercial gloves were considered suitable as testing materials for future CO_2 tests [10]. Although further analysis is needed to corroborate this preliminary conclusion, the artificial ageing was appropriate as, apparently, it allowed a good reproduction of the degradation of the case study.

3.1.2 Consolidants

Several consolidants were selected for impregnation experiments with $scCO_2$, based on previous consolidation tests (Appendix V.1) and possible chemical compatibility with the gloves foam. Other properties such as average molecular weight (M_w) and glass transition temperature (T_g) were also considered (Table 3.1). Although most consolidants have a M_w above 1000 (which are mainly insoluble in CO_2, among other features that may influence solubility [1, 27]), it was expected that, due to their polydispersity, the smallest chains of the polymers could be solubilized and thus impregnated into the foam. T_g below 40°C was preferred in order

[9] Raman spectroscopy was not possible due to high fluorescence of the spectra, possibly due to the degradation of the material.

[10] Unaged and aged samples were also analysed by Thermal Gravimetric Analysis and Differential Scanning Calorimetry in an attempt to obtain a more detailed information on their chemical composition, namely to confirm the presence either of a mixture of polymers, a copolymer or a mixture of a polymer with a copolymer. The results were inconclusive, possibly due to crosslinking and/or degradation of the foams. Other analytical methods, such as Gel Permeation Chromatography and Mass Spectrometry, were discarded since it was not possible to dissolve any of the unaged and aged samples, possibly indicating cross-linked foams. Solubility tests were performed in cyclohexane and toluene, which, according to the literature, would solubilize all three polymers in the formulation [71].

to preserve the foams' flexibility[11] and avoid induction of additional stress. Two ethylene-vinyl acetate copolymers were tested: an aqueous emulsion (Evacon-R™, with (25%) and without dilution) and the pure component (EVA), to progressively reduce and understand the influence of a second solvent (H_2O) in the CO_2 stream. Since vinyl acetate is the component with adhesive properties in those copolymers, poly(vinyl acetate) (PVAc) was also tested due to its known solubility in CO_2 [27, 28]. Paraloid™ B72 (PB72) is a frequently used adhesive in the conservation field, which stability towards photooxidative and thermal degradation has been studied by several authors [72-75], and it was tested for that reason. Regalrez™ 1094 is also a common conservation adhesive, selected for its low molecular weight and compatibility with natural and synthetic isoprene [76].

Table 3.1 – Properties of the selected consolidants according to the respective technical data sheet (Appendix V.2 Consolidants)

Consolidant	Evacon-R™	EVA[12]	PVAc	Paraloid™ B72	Regalrez™ 1094
Chemical composition	Poly(ethylene-*co*-vinyl acetate)		Poly(vinyl acetate)	Poly(ethyl methacrylate-*co*-methyl acrylate) (30/70)	Fully hydrogenated hydrocarbon resin
T_g (°C)	ND	-40 to -30	30	~40	40
M_w	ND	ND	~167 000	~70 000	850

T_g – glass transition temperature; M_w – average molecular weight; ND – not detailed

3.2. Assessment methodology

An identical characterization was performed to all samples, before and after the respective CO_2 test. Macro and microscopic visual characterizations were performed by macroscopic photography, stereomicroscopy and optical microscopy. Dimensional, gravimetric and colorimetric variations were also assessed. Chemical alterations were followed by ATR-FTIR and Raman spectroscopies, the latter one only possible for the unaged samples, due to the fluorescence phenomena observed in the spectra of the aged samples, completely masking the foam spectrum. All characterizations were performed *in-situ*, except for ATR-FTIR to the aged samples, which required sampling. Therefore, infrared analysis was always the first characterization before CO_2 and the last one to be performed after treatment. Further description of the methods and instruments used for characterization is presented in Appendix V.3. The chosen consolidants were also analysed by ATR-FTIR to detect their presence in the foams after treatment (Appendix VI.4.2).

[11] Besides the increased rigidity of the degraded foam, it is important to consider that photo-oxidation processes initiate at the materials' surface and extend to its interior with continued exposure to degradative factors. Depending on the extent of degradation, it was considered that some of the characteristic flexibility may still be preserved in its interior.

[12] EVA with 40 wt. % of vinyl acetate.

3.3. Supercritical CO_2 experiment conditions

Supercritical CO_2 experiments were performed in a laboratory scale high-pressure apparatus (Figures V.3.1 and V.3.2 in Appendix V.3) for test samples and are summarized in Table 3.2. As previously described, the conservation treatment of foams with CO_2 is an innovative method. Therefore, the experimental approach in the present work followed a primary assessment of the safety of $scCO_2$ in discontinuous and continuous conditions, first in unaged and then aged samples. The tested conditions were based on the examples detailed in a Superwood patent [77]. Based on previous cleaning tests with CO_2 performed by Sousa *et al.* [78, 79], the safety of a continuous $scCO_2$ stream with water (0.25%) was also evaluated for an aged sample, along with its efficacy for an eventual cleaning treatment prior to consolidation. Similar parameters were applied in the $scCO_2$ and $scCO_2 + H_2O$ tests, excepting for the decompression times. These were slowly decreased throughout the experiments to avoid inducing damages to the material, to evaluate its resistance to pressure drop and to, subsequently, optimize the process. The following experiments focused on a preliminary study on the safety and efficacy of several impregnation treatments with the chosen consolidants in aged samples. Saturated supercritical streams in two different conditions (A and B) were tested, in which the influence of pressure of 200 and 280 bar at 40 °C was investigated. A more detailed description of the CO_2 experiments is presented in Appendix V.3.10.

Table 3.2 – Experimental conditions of the $scCO_2$ tests in the foam samples, with and without the use of a co-solvent (H_2O) and several consolidants. Discontinuous and continuous conditions were investigated, along with variation of T, p and experiment time

	Test	Sample	Conditions		Additional compounds	Time (min)		
			T (°C)	p (bar)		Comp.	Exp.	Decomp.
1	Discontinuous stream	K1NA	33	100	-	40	30	120
2		K1A			-	40	30	90
3	Continuous stream	R1NA	33	90	-	30	30	15
4		N1A			-	30	30	15
5	Co-solvent (continuous)	K1A	33	90	H_2O (0.25%)	20	40	10
6	Impregnation (Conditions A, discontinuous)	N1A	40	200	Evacon (25% in H_2O, 2 mL)	10	120	5
7		R1A			Evacon (100%, 1 mL)	10	120	15
8		K2A			PB72 (0.75 g)	10	120	25
9		K3A			EVA (0.75 g)	15	120	15
10	Impregnation (Conditions B, discontinuous)	N2A	40	280	EVA (0.3 g)	10	120	15
11		R2A			PB72 (0.47 g)	15	120	15
12		K4A			Evacon (100%, 0.5 mL)	10	120	15
13		N3E			PVAc (0.5 g)	10	120	10
14		K5E			Regalrez 1094 (0.5 g)	15	120	15

Comp. - compression; Exp. – experiment time at constant T and p conditions; Decomp. - decompression

Chapter 4. Results and Discussion

Characterization of the test samples, before and after CO_2 treatment, is summarized in Table 4.1 and discussed below. The full data set is detailed in Appendix VI.

Table 4.1 – Summarized results of the characterization of the treated samples after CO_2 experiments

	CO_2 experiment			Visual and physical alterations	Δ *Mass* (%)		Δ *E**		Spectra alterations
	Test	Sample	Additional substances		1	2	A	B	
1	Discontinuous stream	K1NA	-	No	-0.15	-0.13	1.14	1.14	No
2		K1A	-	No	-0.20	-0.09	1.26	1.37	No
3	Continuous stream	R1NA	-	No	-0.62	-0.47	0.78	0.60	No
4		N1A	-	No	-0.38	-0.30	1.75	1.22	No
5	Co-solvent	K1A	H_2O	No	-0.24	0.10	1.14	0.62	No
6	Impregnation A	N1A	Evacon (25%)	No	-0.10	-0.36	4.66	3.09	No
7		R1A	Evacon (100%)	No	2.15	2.18	0.60	2.26	No
8		K2A	PB72	No	-0.27	-0.27	0.82	2.12	No
9		K3A	EVA	No	-0.08	-0.21	1.25	1.02	No
10	Impregnation B	N2A	EVA	No	-0.40	-0.36	1.03	0.47	No
11		R2A	PB72	No	-0.73	-0.57	1.30	1.50	No
12		K4A	Evacon (100%)	No	-0.32	-0.37	1.41	1.30	No
13		N3A	PVAc	Yes	-0.28	-0.27	6.11	6.78	Yes
14		K5A	Regalrez 1094	No	-0.01	-0.03	3.77	4.35	No

4.1. Safety assessment

In general, the experimental results indicate that visual, physical and chemical alterations were not relevant for most samples after CO_2 treatment.

Regarding visual analysis and dimension measurements (Table 4.1 and Table VI.1.1 in Appendix VI.1), most samples did not suffer significant alterations after treatment and no major changes were detected while in the CO_2 chamber during experiments. This inalterability may suggest that either the polymers' swelling due to CO_2 interaction was not relevant enough to be visually detected (possibly related with the porosity of the foam) or that CO_2 did not interact with the material and, consequently, swelling did not occur. However, both dimensional and rigidity (by touch) alterations were exceptionally detected for sample N3A, possibly due to the impregnation of PVAc, as it will be further explored in Section 4.2.

Valid for most samples, gravimetry results (Table 4.1 and Appendix VI.2) show a pattern in weight variation post-treatment of an overall decrease below 1%, characterized by an initial decrease in weight in the first measurement, followed by a small increase in the second one. This tendency was attributed to a possible ability of the CO_2 to remove water from the foam (material with hydrophilic nature), which may be reincorporated from exposure to environmental humidity after treatment. The results from samples R1NA and R2A corroborate this hypothesis by showing the highest decrease in weight. Since both foams are from Reusch test gloves (the only pair of gloves previously used – mechanical wear), a higher content of water and salts incorporated from sweating was already expected before treatment. Gravimetry data also suggest that the continuous stream may have promoted more water removal from the foams when compared with the discontinuous stream, resulting in a higher decrease in weight (average[13] of -0.50% compared to -0.18%). Similarly, the same effect was verified in impregnation tests with the increase in pressure from 200 bar in Condition A to 280 bar in Condition B (average[14] of -0.15% and -0.36%, respectively), possibly related to an increase in the CO_2 density[15]. Also, on the impregnation tests, the significant weight increase for sample R1A was attributed to the verified expansion of the consolidant during depressurization and subsequent direct contact with the sample underneath. Other weight discrepancies, such as the results of samples N1A (second treatment) and K4A second measurements, may be related to higher variations in relative humidity, which influences the quantity of water absorbed or not by the foam and its weight.

Regarding colorimetry measures, the just-noticeable total colour difference (ΔE^*) is 2.3, meaning that colour change is perceptible to the naked eye above this value [81]. Results shown in Table 4.1 (and in Tables VI.3.1 and V.3.2 in Appendix VI) were, predominantly, not noticeable for both colour measures performed for each sample and variations occurred heterogeneously in L^*, a^* and b^* variables. However, exceptions were also detected, and colour variation was perceptible for three samples (N1A – second treatment, N3A and K5A) submitted to impregnation tests. Considering that no other alterations were detected during characterization, the significant colour difference for N1A (namely towards negative a^* and b^* values, i.e., less red and yellow, respectively) was attributed to a loss of fragments at the fragile degraded surface, observed in Figure 4.1. This

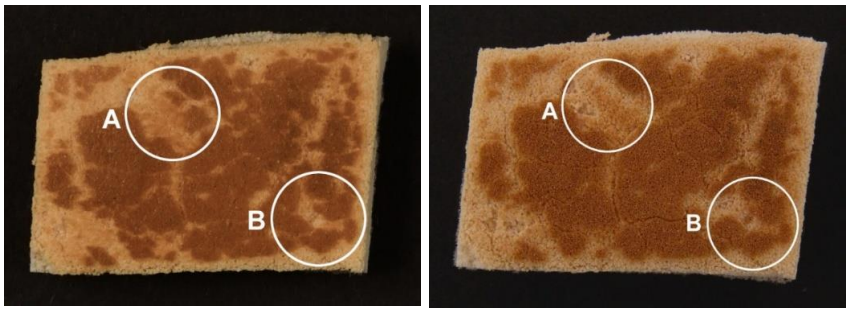

Figure 4.1 – Colour comparison (areas A and B) for sample N1A, before (left) and after (right) treatment with Evacon (25%). Loss of several fragments in both areas is detectable, which may have contributed to the significant colour difference presented in Table 4.1.

[13] For comparison purposes, only the first measurement was considered for calculation of the arithmetic mean, which was performed immediately after removing the samples from the CO_2 chamber.

[14] Only the first measurement was considered, which was performed within the same time period after treatment (one day after) for all samples. For Condition A, it was excluded the result of R1A (mass increase possibly due to an expansion of the consolidant), and N3A was excluded from Condition B average, which impregnation was considered successful (further details in Section 4.2).

[15] Density of carbon dioxide at 200 bar is 0.83981 g/mL and 0.89853 g/mL at 280 bar [80].

could also have been promoted by negligent handling between treatments and characterizations. Gravimetry results also indicate that this analysis may not be appropriate for safety assessment, unless severe loss of material occurs, as no significant variations were detected. On the other hand, the Tyndall effect was observed during the experiment with samples N3A and K5A[16], suggesting the solubilization of the consolidants. Colorimetric variation detected for sample N3A may be thus related to the successful impregnation of PVAc (Section 4.2) since no material losses were detected (Figure 4.2, top). Regarding sample K5A, this variation is probably not related to a negligent handling or an impregnation, since no loss of fragments or consolidant were detected after the experiment (Figure 4.2, bottom). However, the treatment could have had a cleaning effect, which may explain the increase in ΔL^* in both measurements (Table VI.3.2 in Appendix VI) or could have chemically interacted with the foam while solubilized in CO_2. However, more research is needed to understand this result.

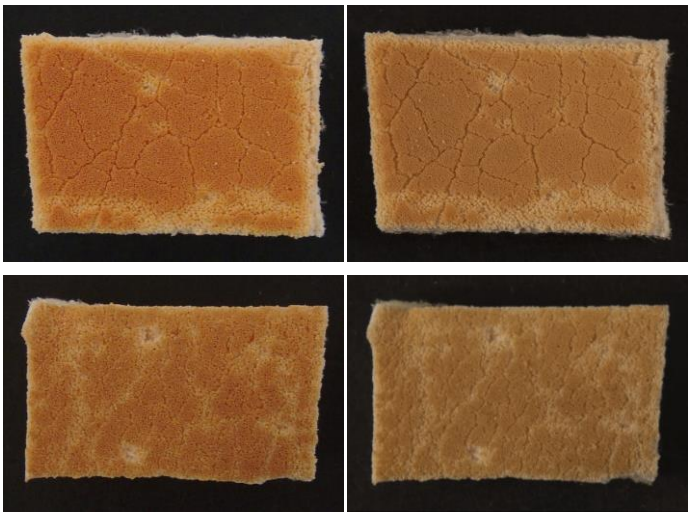

Figure 4.2 – Samples N3A (top) and K5A (bottom), before (left) and after (right) treatment with PVAc and Regalrez, respectively.

Raman and infrared spectroscopies (Table 4.1 and Appendix VI.4 and VI.5) did not detect chemical alterations after treatments for any sample, regarding the foams' molecular structure as well as the presence of carbon dioxide. However, spectral alterations were detected in the impregnation test of sample N3A, attributed to the presence of the consolidant (Section 4.2).

Contrary to what might have been expected, the characterization results indicate that the tested treatment conditions did not seem to affect the physical and chemical stability of the foams regardless of the conditions used, although further testing and analysis are needed to confirm the safety of the method. Also, no discrepant behaviours were detected between samples from different brands, which suggests that differences in the polymers' monomers content may not significantly influence the responsiveness of the material to the CO_2 after ageing.

4.2. Efficacy of the impregnation tests

A successful solubilization of the consolidants in CO_2 was not possible to confirm in all experiments. Since all tests aimed for a saturation point of the substances in CO_2, it was not expected a total solubilization of the introduced quantity of consolidant inside the chamber and, thus, the visual perception of its solubility. On the other hand, all consolidants expanded and transformed into white amorphous rubbers during

[16] Effect of light scattering in a colloidal dispersion. In both impregnation experiments, this phenomenon characterized by a cloudy orange effect inside the CO_2 chamber at the experiment conditions.

depressurization, indicating a possible sorption of CO_2 and modification of the substances' polymorphism, but preventing the assessment of their weight variation pre and post treatment. However, as previously stated in the Introduction, the Tyndall effect (usually occurring when there is a solubilization of a substance that leads to the scattering of the light) was observed in the impregnation tests with PVAc and Regalrez. This is in agreement with what was expected, since PVAc is reported to be soluble in CO_2 and Regalrez has a low M_w.

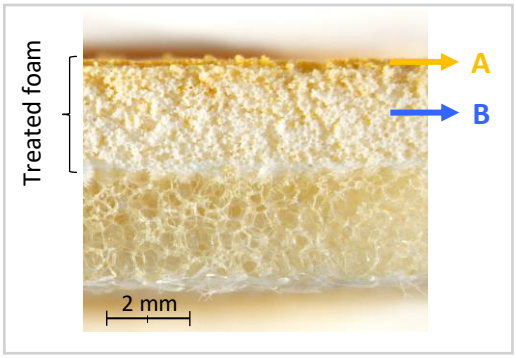

Figure 4.3 – Cross section of the sample N3A, where the extension of the more degraded (A) and less degraded (B) areas is observed.

Visual and molecular characterization with infrared spectroscopy (Figures 4.3-4.5 and Appendix VI.4) indicates that only PVAc was detected at the surface of the sample after treatment. The extension of the consolidant's presence in the sample N3A was evaluated by infrared analysis on samples collected from several sections of the foam, namely more degraded (top and shallow interior) and less degraded (lateral exterior and central interior) areas (Figure 4.3). Infrared results (Figure 4.4) indicate that PVAc is only present at the degraded part of the foam (top and shallow interior), also confirmed by optical microscopy analysis (by comparison with an untreated sample, as shown in Figure 4.5, A and B), particularly in smaller pores. To explain the more superficial impregnation of PVAc in the foam after treatment, several hypotheses have been posed. The first suggested hypothesis is a precipitation of the consolidant on the foam during depressurization, through a decrease in its solubility in CO_2 with pressure drop. Another hypothesis is a possible different morphology between the degraded surface of the foam (characterized by a more porous structure, Figure 4.5) and less degraded areas (less porous). In this case, an in-depth diffusion of CO_2 into the foam may have been prevented, leading to a superficial deposition of PVAc. Another possible explanation is that impregnation may have also been achieved through the establishment of a chemical bond with the degraded surface (favoured

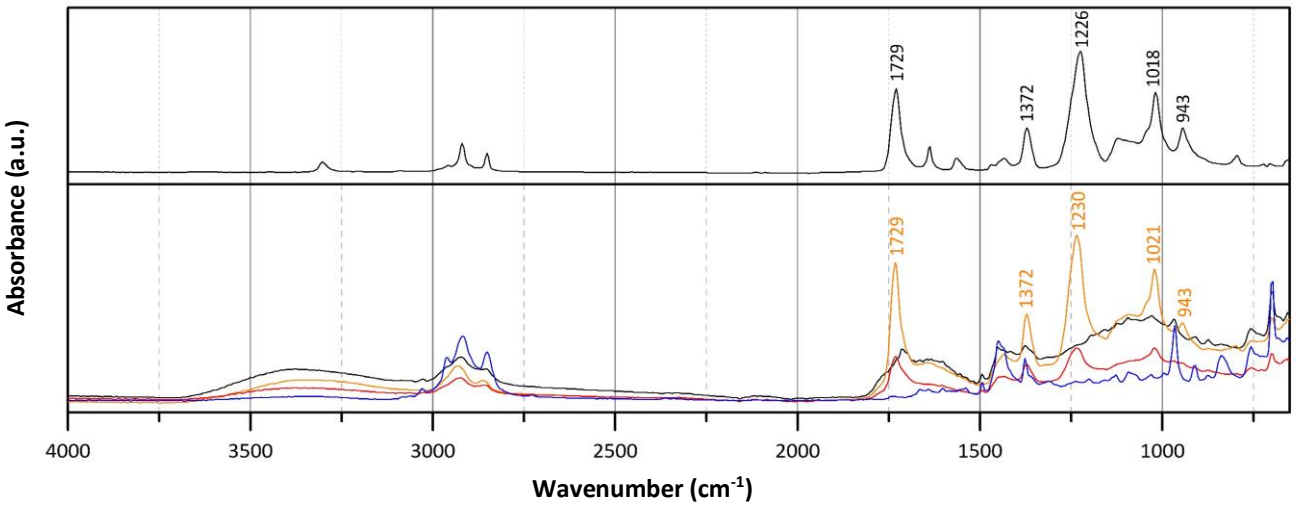

Figure 4.4 – Infrared spectra of PVAc (top) and the superficial degraded foam of sample N3A (bottom), before (black) and after (orange) treatment. Spectra of the degraded shallow interior (red) and less degraded deep interior (blue) of the sample after treatment is also presented, showing that PVAc is only present at the degraded area of the foam.

Figure 4.5 – OM images in darkfield (200x) of an untreated sample (A) and treated samples with PVAc (B) and Regalrez (C). After impregnation tests, only the presence of PVAc was detected, particularly in the smaller pores (red circles).

over the less degraded), possibly due to a higher affinity of PVAc with degradation products of the foam, namely moieties with carbonyl groups.

As shown in Table 4.1, it was possible to detect some alterations in sample N3A, which were attributed to the presence of the consolidant. An increase in its cohesion and rigidity (assessed by touch) was detected, along with a decrease in its dimension, of approximately 1mm (Appendix VI.1). Moreover, the characteristic shine of the consolidant (Figure 4.5, B) may have influenced the colour variation detected after treatment. However, contrary to what may have been expected, no weight increase was detected, since it may have been compensated by the removal of water from the foam during CO_2 treatment that leads to a decrease in weight.

As for the impregnation test with Regalrez, the observed Tyndall effect during depressurization and the significant colour variation after treatment strongly suggested a successful impregnation. However, infrared analysis (Appendix VI.4) was inconclusive, due to overlapping of the characteristic bands of the consolidant with the bands from the foam, and its presence was also not detected in any section of the sample when observed under the microscope, namely in the pores of the degraded surface as observed with PVAc (Figure 4.5, B and C). Thereby, is was concluded that, although the consolidant may have solubilized in the CO_2 and interacted with the foam, or even impregnated it during treatment, it was not able to stay inside the sample, possibly due to a too slow depressurization time.

Results from the other impregnation tests indicate that, in the tested conditions, the consolidants were not successfully solubilized in CO_2, and, therefore, were not carried to the interior of the samples. Although they all exhibited an ability to absorb CO_2 (due to their expansion), the results suggest an inadequacy of the tested parameters for their solubilization in CO_2. Incompatible chemical characteristics may also explain the insolubility of most consolidants, particularly their high molecular weight. The expected solubilization of the smaller segments of the polymers (due to polydispersity), either did not occur or was not relevant enough to be detected. Moreover, as described in the Introduction, the presence of other features that increase the solubility of a substance in CO_2 (such as a flexible backbone, high free volume, weak interactions between the polymer segments and presence of carbonyl groups), may explain the successful impregnation of PVAc despite its relatively high molecular weight (approximately, 167 000).

Chapter 5. Conclusions

The present study was a preliminary research for the development of a new approach for the preservation of modern and contemporary cultural heritage. It focused on the novel application of supercritical carbon dioxide in the consolidation treatment of foams, such as the blend of polyisoprene, polybutadiene and polystyrene in Robert Enke's pair of gloves. The research comprised the gathering of the relevant information found in the supercritical fluids' literature for the application of the method to this purpose and presents an insight on the case-study's materiality and significance. The resulting knowledge base was of utmost importance to design a conservation plan to preserve what was identified as the authenticity of this object.

The method was considered safe for the foam samples under the tested conditions. Although the sorption of CO_2 by the treated foams was expected, the present work aimed to find suitable treatment conditions that would minimize this effect and, thus, avoid irreversible damages due to the swelling of the foam. The obtained results did not reveal permanent dimensional variations in any of the treated foam samples. Also, no other visual, physical or chemical alterations were detected due to interaction with the CO_2, co-solvent or consolidants that could compromise the safety of the foams. The colour variation of the foam sample treated with Regalrez 1094 was the only exception, but further testing is needed to understand this result. Regarding the efficacy of the method, PVAc was successfully impregnated at 40°C and 280 bar in all the extension and thickness of the degraded foam surface, indicating that a homogeneous penetration with minimal interaction may have been achieved. It is suggested that the consolidant may have precipitated during depressurization or it established a chemical bond with the degradation products, namely carbonyls.

Most analyses of the performed characterization provided useful information regarding the safety and efficacy of the experiments. Optical microscopy complemented with infrared spectroscopy revealed to be a particularly useful analysis for assessing the presence of the consolidant in the foam. Gravimetry analyses was the only exception, since a scale with higher sensibility is required for safety assessment to detect smaller mass variations of the foams. Moreover, the assembling of a photography studio could also be helpful for future macroscopic characterization, to guarantee an easier reproducibility of the pre and post-treatment images.

In future research, it is a priority to confirm the obtained results through the repetition of the performed experiments and test different conditions to optimize the process, at least for the impregnation with PVAc. Considering that the thickness of degraded areas depends upon the object itself, samples with different extents of degradation should also be tested to assess the penetration of the consolidant. Future experiments should also include a more detailed characterization of the samples to assess the safety and efficacy of the method. Scanning Electron Microscopy (SEM) may be useful to obtain high resolution images of the topography of the foams and detect the presence of the consolidant, even at small concentrations, and access

the homogeneity of its application. Cretté *et* al. [40] have proven that Structured Light 3D Scanning may be a valuable tool to accurately observe dimensional alterations, which can complement or even substitute the performed dimensional characterization. Additionally, since an increased cohesion and mechanical resistance are expected in a successful consolidation, it is also crucial to include mechanical testing in further research. These tests were not performed in the present work since a disparity of results due to the fragile nature of the material was already expected and a great number of testing would be necessary for conclusions. The aim is to assess the efficacy of the CO_2 for the impregnation of a consolidant in-depth, by the comparison of the resistance of the material before and after treatment. Another goal is to evaluate the possibility that the presence of PVAc at the degraded surface of the foam may induce further delamination between this area and the less degraded material beneath. Further experiments should also strive to assess long-term safety and efficacy through the accelerated ageing of the tested samples, particularly of the successful impregnation experiments. Although it is expected an irreversibility of a consolidation treatment, it is of the utmost importance to guarantee the future re-treatability of the material, in case of failure of the consolidant adhesive properties.

Research is still needed to conclude the safety and efficacy of the treatment, along with optimization of the process in order to be applied in the preservation of foams present in cultural heritage. However, it is expected that the present work may be a starting point for the development of a novel consolidation approach for foams and, hopefully, for a wider range of plastics. Furthermore, considering the ability of CO_2 to remove water, and possibly salts, from the studied foams, future researches may also explore the application of this method as an option for extractions or disinfection of fungi.

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Appendices

APPENDIX I. Degradation of plastics due to physical, chemical and biological factors

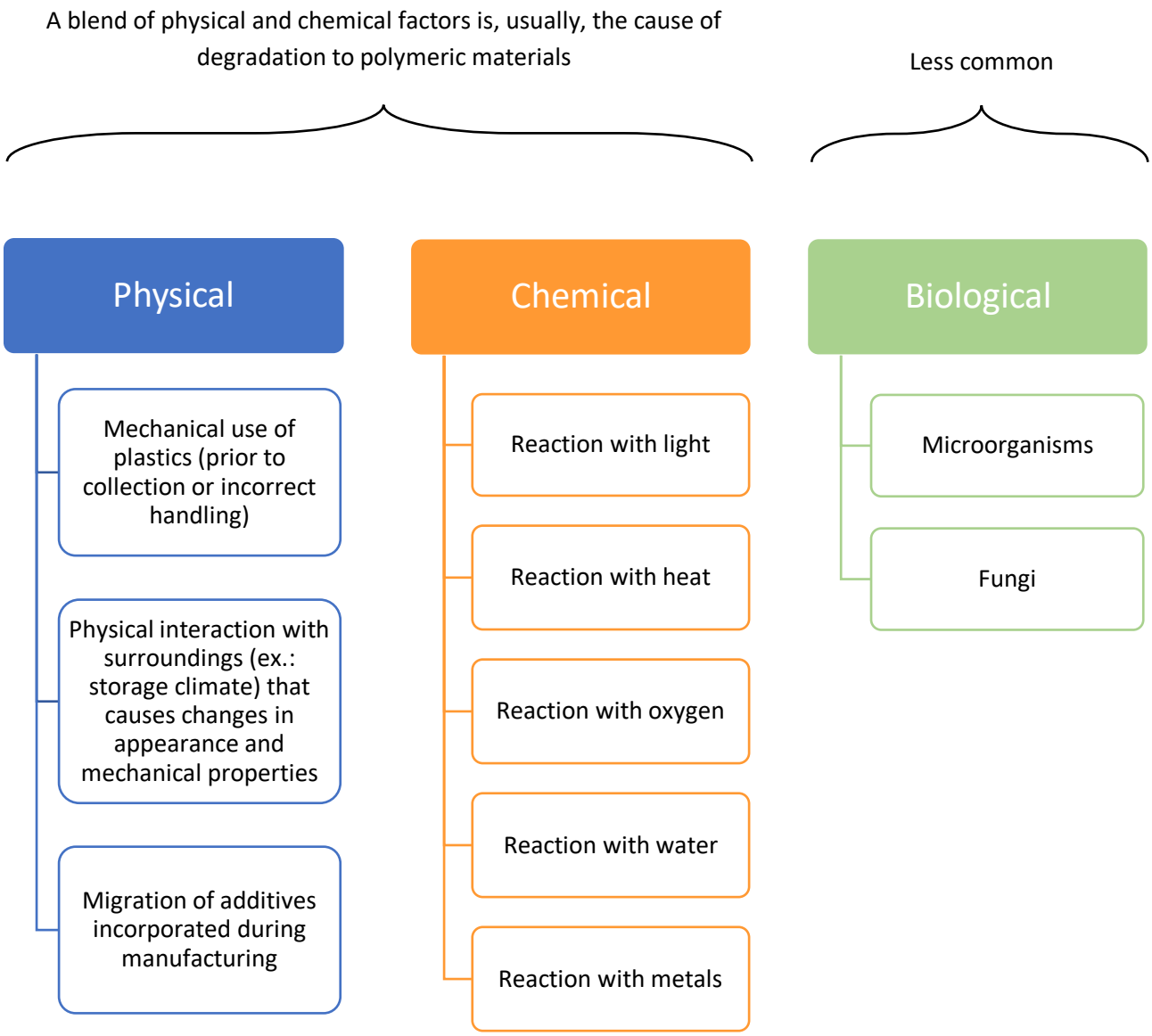


Figure I.1 - Causes of degradation of plastics in museum collections attributed to physical, chemical and biological factors, according to Shashoua [4].

APPENDIX II. Technical sheet of the case-study

Designation: Robert Enke's Pair of Goalkeeper Gloves.

Category: Sports equipment.

Typology: Goalkeeper gloves.

Current owner: *Museu Benfica - Cosme Damião, Sport Lisboa e Benfica*.

Date of acquisition: November 14th, 2016.

Location: *Departamento de Reserva. Conservação e Restauro*, *Museu Benfica - Cosme Damião*, *Sport Lisboa e Benfica* sports' complex, Eusébio da Silva Ferreira Avenue, 1500-313, Lisbon.

Owning chronology: Original owner - Robert Enke (from ? to 2000/2001); second owner - Guilherme Cabral (from 2000/2001 to November 14th, 2016); current owner - *Museu Benfica - Cosme Damião* (from November 14th, 2016 to the present date).

Provenance history: Robert Enke acquired this pair of gloves while playing as a goalkeeper at *Sport Lisboa and Benfica* between the 1999/00 and 2001/2002 seasons, possibly for training. Although the year of acquisition is unknown, the player signed and donated the gloves to Guilherme Cabral's uncle, who offered them to Guilherme as a birthday present by his 9th or 10th anniversary (2000 or 2001). After keeping the gloves for almost 17 years and noticing the tenacious importance of Robert Enke to the sports club, the well-known supporter decided to donate them to *Museu Benfica – Cosme Damião* for proper conservation and storage, or even exhibition. Not only representing the only item of the player owned by the institution, the donation was also expected to encouraged other supporters to actively contribute to the quality of the museum by donation of relevant objects for the history of Benfica.

Description: The pair of gloves can be divided in two main parts: the hand and the fist area. The former one, as it can be seen in Figures II.1 and II.2, has a different material construction on the palm and back side. The palm area is totally covered by a synthetic latex foam and both gloves have Robert Enke's signature and an inscription dedicated to Guilherme Cabral (*Para o Gui*) with a black ink. The back side is mainly covered by a single piece of black foam, which seems to be the same material covering the middle, ring and little fingers in embossed triangular shapes. The edges of these fingers, thumb and half of the back side are covered by a silver film, apparently, over a foam. On the other hand, the fist area has an elastic band and Velcro strap to allow a personalized adjustability. Similar to the hand part, the same synthetic latex foam and black material covers the front and back side, respectively. In this last area, there is also an identifying beige fabric with Robert Enke's name.

Dimensions: length 27.4 cm, width 17.7 cm, thickness approx. 2 cm.

Brand: Possibly Reusch, according to the information given by the Documentation and Information Centre of *Museu Benfica* and the Department of Product and Design of Reusch (Section 2.1).

Materials: A preliminary characterization based on infrared spectroscopy was performed by Dr Susana França de Sá [46]. The study concluded that a synthetic latex covers both palm and back side (the latter one with an additional black colourant), possibly composed by a mixture of polyisoprene and poly(butadiene-styrene) (Section 2.1). Additionally, the silver material on the back side is a polyurethane film and the Velcro strap is polyamide. The composition of the black ink was inconclusive.

Figure II.1 - Back side of Robert Enke's pair of gloves (© *Museu Benfica - Cosme Damião*).

Figure II.2 - Palm side of Robert Enke's pair of gloves, where it is possible to observe the signatures and inscriptions by the player.

APPENDIX III. Condition report of the case-study's foam

III.1 Identified damages and possible causes

Table III.1.1 – Description, possible causes and examples of the damages identified on the studied foam

Damage	Description	Possible cause(s)	Appearance
Yellowing	Widespread yellow tone over the entire foam, particularly at the surface area.	Chemical degradation of the foam and formation of chromophores and conjugated double-bonds.	
Superficial material losses	Areas of a lighter tone and reduced superficial gloss, corresponding to areas where inner layers of the foam are visible.	Augmented fragility and loss of flexibility due to chemical degradation, possibly allied to an increased susceptibility to abrasion.	
Cracks and fractures	Superficial and deep lines of structural failure. Mainly affecting the areas of most use and impact of the ball, such as the finger joints, palms and, particularly, the right thumb.	Physical damage due to the chemical degradation of the material, leading to loss of flexibility and rigidity. Their location suggests the influence of mechanical damages during use, such as the impact of the ball and movement of the hands.	

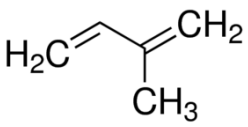
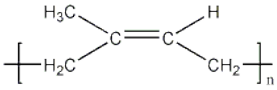
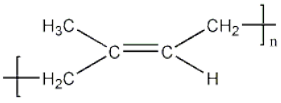
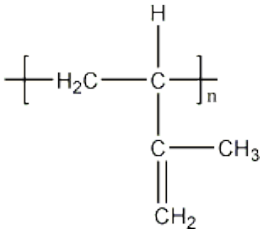
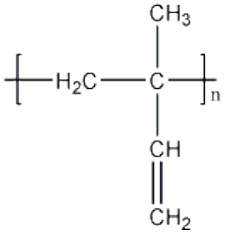
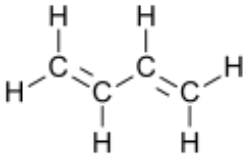
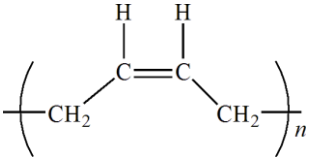
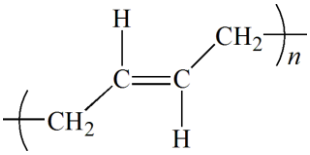
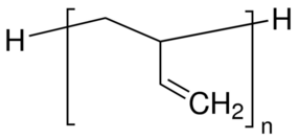
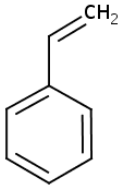
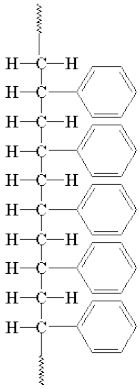
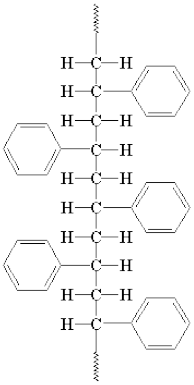
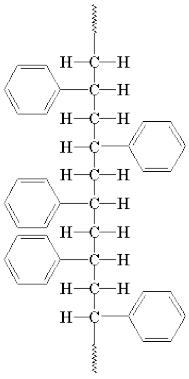
Fragments in detachment	Crumbling and loose fragments from the main structure and in risk of loss. The most affected areas are the fingertips, particularly the right thumb, and right palm.	Aggravation of the cracks and fractures due to chemical and physical damages.	 
Lacunae	Complete material loss (foam layer). Mainly affecting the right glove in the thumb area and the fingertips of both palms. One other lacuna is visible at the left bottom area of the right palm.	Detachment of fragile and loose fragments. Lacunae at the fingertips show rounder and low-profile ends, indicating that abrasion may be the main cause of the damage at these areas.	 
Deformations	Physical distortions, namely a bended right thumb (that can lead to an eventual rupture) and several curled areas at the lower part of the palms, fists and fingers.	Mechanical use of the gloves and incorrect storage prior to collection. Loss of flexibility and physical interaction with the surrounding conditions (such as relative humidity), may have contributed to the distortions.	

Material deposit by transfer	Detachment and transferring of the silver material at the back side of the left thumb, to the foam side of the right glove.	Deficient storage prior to collection, leading to a direct contact between the materials. Ageing of both materials may also be related, since the foam is brittle and powdery and the silver material is severely cracked, fractured and, possibly, more viscous.	
Dark stains	Apparently superficial stains of a dark tone, sporadically visible at the bottom of both palms.	Accumulation of dirt particles from use or incorrect storage. Transferring of the inscription's black ink (when written, stored or due to the crumbliness of the material) may also be a possibility.	
Brown stains and spots	Small spots and stains of a brown colour, more intensively present at the left fist.	Biological factors and/or concentration of sweat (humidity and salts), impregnated during the use of the gloves (e.g. passing of the fist on the sweated forehead)	

Cracks and fractures | Fragments in detachment | Lacunae | Deformations | Material deposit by transfer | Dark stains | Brown stains and spots

APPENDIX IV. Chemical structure of isoprene, butadiene and styrene

Table IV.1 – Chemical structure of isoprene, butadiene and styrene monomers and isomers of the respective polymers

Isoprene monomer			
			
***Cis*-1,4 PI**	***Trans*-1,4 PI**	**3,4 PI**	**1,2 PI**
			
1,3 butadiene monomer			
			
***Cis*-1,4 PB**	***Trans*-1,4 PB**	**1,2 PB**	
			
Styrene monomer			
			
Isotactic PS	**Syndiotactic PS**	**Atactic PS**	
			

APPENDIX V. Experimental

V.1 Previous consolidation experiments

A previous research on the conservation treatment of the case-study was performed. Long-term safety and efficacy of two different techniques, nebulization and facing, was studied for the application of three consolidants and one light stabilizer in test samples.

Nebulization and facing techniques were selected for allowing minimal interaction with the fragile foam during treatment, and thus preventing further material loss. Considering the difficult reproduction at a laboratory scale of the complex industrial formulation of the case-study's foam, test gloves were characterized and selected based on possible chemical similarity. For a better representativity and variability of the results, three different glove brands were chosen - Reusch, Nike and Kipsta (Appendix V.2 Materials). Since the chemical composition of the case-study's ink is unknown, four black permanent inks were applied in one glove of each pair, which were then artificially aged[17], in order to study the inks behaviour and simulate the ageing of the case-study. Testing was performed in unaged and aged foam samples.

The consolidants Latex Milk 77200 [18], Evacon-R™ [19] and Mowilith® LDM 7667 [20] were selected based on chemical similarity and possible compatibility with the case-study's foam. Moreover, it was decided that water based consolidants, i.e. water soluble or in the form of emulsions/dispersions, should be used due to most plastics and writing inks susceptibility to organic solvents, which tends to increase following chemical degradation [60]. On the other hand, although relative humidity had a possible influence on the degradation of the foam, water was still considered the safest and most suitable solvent for its non-toxicity and an adequate setting time for the penetration of the consolidants. It was also considered the solubility tests of the writing inks, which were insoluble in water. All consolidants were applied as 25% solutions.

Tinuvin® B 75 [21], a light and heat stabilizer, was then added to all consolidants' solutions, to enhance their chemical and physical properties, by avoiding or decreasing their photo degradation. It was solubilized in isopropanol, which was the least toxic solvent that was simultaneously compatible with the polymers of the foam and black inks (assessed by solubility tests). These solutions were only applied by the facing method, which results were compared to the non-stabilized solutions.

[17] To simulate the degradation conditions of the case-study, namely exposure to oxygen, UV radiation and humidity (from sweat), the test gloves were firstly aged in a SolarBox, followed by exposure to relative humidity cycles in an oven.

[18] Latex Milk is a natural rubber latex, kept liquid with ammonia and pre-polymerized.

[19] Evacon-R™ is a non-plasticized aqueous copolymer dispersion, based on vinyl acetate (adhesive component) and ethylene (which improves flexibility and compatibility with the substrate). It was specifically developed for the conservation field, particularly as an adhesive for paper conservation, having passed in the Silver Tarnish and PAT tests. It is a stable, non-plasticised and reversible adhesive, with a neutral pH and resistant to acid hydrolysis due to the presence of calcium carbonate ($CaCO_3$) in its composition.

[20] Mowilith® LDM 7667 is a non-plasticized aqueous copolymer dispersion, based on (meth)acrylic acid esters (adhesive component) and styrene (component improving compatibility with the substrate).

[21] Tinuvin® B75 is a synergistic blend of 20% Irganox® 1135 (antioxidant), 40% Tinuvin® 571 (UV absorber) and 40% Tinuvin® 765 (HALS, hindered amine light stabilizer).

Solutions of each consolidant and consolidant+stabilizer were applied to unaged and aged samples, the latter ones submitted to a second ageing cycle for evaluation of the solutions safety and efficacy in the long-term. Unaged and aged reference samples, which were not submitted to any treatment, were also included in the research for comparison of the results.

The samples were characterized before and after treatment by colorimetry, peeling-test[22] and ATR-FTIR. Based on the infrared results, the O-H stretching bands area variation (3680-3100 cm^{-1}) was calculated to assess the efficacy of the stabilizer in protecting the foam and the consolidants.

Mowilith 7667 was the consolidant with the best long-term results when applied with Tinuvin B75®. In the peeling-test, it showed satisfying results in enhancing the cohesion of the foam, when compared to the reference samples. It also had the lowest area variation in the O-H stretching bands, which indicates an efficient blocking of the formation of degradation products and suggests a good compatibility with the stabilizer. Evacon-R™ also presented satisfying results. Regarding the application techniques, nebulization proved to be a safe method, contrary to facing, which induced material loss of the fragile foam. Also, both methods did not guarantee a homogeneous and in-depth penetration of the consolidant, compromising the efficacy of the treatment.

V.2 Materials

V.2.1 Unaged and aged test gloves

Figure V.2.1 – From left to right: Reusch and Kipsta gloves before artificial ageing. The Kipsta right glove was at exhibition at the store, which explains the visible dirtiness and slight yellowing when compared to the left one.

[22] Manual system of an acetate paper sheet with an adhesive tape. A pre-determined area of adhesive tape was pressed on top of the samples and the area of detached particles was accounted to evaluate and compare the cohesion of each sample.

Figure V.2.2 – From left to right, top to bottom: Nike, Kipsta and Reusch gloves after artificial ageing.

V.2.2 Consolidants

Table V.2.1 – Data on the selected consolidants as detailed in the respective technical data sheets

	Evacon-R™	**EVA**	**Paraloid™ B72**	**PVAc**	**Regalrez 1094**
Product/supplier	EVACON-R™ / Conservation by Design (CXD)	Poly(ethylene-*co*-vinyl acetate) #340502 / Sigma-Aldrich	Paraloid™ B72 #67400 / Kremer Pigmente	Poly(vinyl acetate) #182486 / Sigma-Aldrich	Regalrez™ 1094 / Eastman
Form	Liquid (aqueous emulsion)	Beads	Pellets	Pellets	Granulated resin
Solubility	Dilution in water	Toluene, Tetrahydrofuran (THF) and methyl ethyl ketone (MEK)	Alcohols, chlorinated hydrocarbons, esters and ethers	Ketones, ethers and aromatic hydrocarbons	Aliphatic and aromatic solvents, C5 and higher esters and ketones
Toxicity	Non-toxic	Non-toxic	Non-toxic	Non-toxic	Non-toxic

V.3 Instruments and methods

V.3.1 Sample preparation

Foam samples, with an average dimension of 1x1,5 cm, were cut from the three selected test gloves, both unaged and artificially aged. They were labelled with the first letter of the correspondent glove ('R' for Reusch, 'N' for Nike and 'K' for Kipsta), followed by a number and 'NA' or 'A', for unaged or aged, respectively. Samples required no further preparation and were randomly selected for the experiments.

V.3.2 Sampling for infrared spectroscopy

Samples were collected from the previous foam samples to reduce the damage and material loss of the degraded surface induced by the required mechanical pressure for ATR-FTIR analysis.

V.3.3 Stereomicroscopy

Stereomicroscopy images were acquired using Leica MZ16 (magnifications between 10x and 80x), coupled to Leica ICD digital camera, Leica KI 1500 LCD fibre-optic light system and Leica FireCam software. Images were used to complement macro photography for the characterization of the macro morphology of the samples pre and post treatment. For each sample, a mapping mask (in acetate sheet) with the location of all photographed areas was done before treatment, to enable their replication afterwards.

V.3.4 Optical Microscopy

The foam samples were observed in a Zeiss Axioplan 2 microscope equipped with a transmitted and incident halogen light illuminator (tungsten light source, HAL 100) and UV light (mercury light source, HBO 100 illuminator), coupled to Nikon DXM1200F digital camera, with Nikon ACT-1 application program software. Samples were analysed with 10x ocular lenses and 10x/20x/50x objective Epiplan lenses (giving total magnification of 100x, 200x and 500x, respectively). Samples were monitored with incident light (normal light), including darkfield and crossed-polarized light, and with UV light, to monitor any superficial alteration and detect the presence of the consolidants. The scales were calibrated within the Nikon ACT-1 software. Only images acquired in dark-field provided relevant information and are presented in this work.

V.3.6 Mass variation

Sample weight determinations were obtained with a Sartorius Lab Instruments GmbH & Co. KG micro analytical scale. Calibration of the equipment was performed before each weighing. Pre-treatment measurements were performed immediately before placing the sample inside the CO_2 chamber. Post-treatment measurements were performed in two distinct moments: 1) first weighing immediately after removing the sample from the CO_2 chamber or, for impregnation experiments, one day after (due to the presence of CO_2 inside the foam as a result a longer experiment time at constant conditions – 2h); 2) second weighing at a maximum of three days after. Percentual mass variation was determined by comparison of the pre-treatment with both post-treatment measurements

V.3.5 Dimension variation

Macroscopic images of the samples were taken on a millimetric paper, before and after treatment. Dimension variation was assessed by comparison of both measurements.

V.3.7 Colourimetry

Colorimetric measurements were performed using a *Datacolour International* colourimeter (*Microflash*), which optical system uses a diffuse illumination from a pulsed Xenon-arc lamp over a 10mm diameter measuring area, 10° viewing angle geometry and D65 illuminant. Calibration with white and black standard plates was performed before each measurement. *Lab** coordinates were measured in two predetermined areas, A and B (three measurements each), on top of each sample before and after treatment. Average and standard deviation were calculated for each *Lab** coordinate, along with the variation (*Δ*) of each coordinate before and after treatment. Total colour variation (*ΔE**) was also calculated according to the CIE 1976 formula (Equation 1), which values above 2.3 were considered just noticeable differences [81].

$$\Delta E^* = \sqrt{(\Delta L)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Equation 1.

V.3.8 Infrared Spectroscopy in Attenuated Total Reflection (ATR-FTIR)

Infrared spectroscopy in attenuated total reflection (ATR-FTIR) was carried out with the Handheld 4300 Agilent spectrophotometer, equipped with a ZnSe beam splitter, a Michelson interferometer and a thermoelectrically cooled DTGS detector. This ATR interface allows the analysis of samples with a minimum size of 200 microns. Spectra were acquired with a diamond ATR interface, 32 scans and 8 cm^{-1} resolution, and spectral analysis was performed using OriginPro 8 software. Spectra are presented as acquired, without baseline corrections or normalizations.

Due to the necessity to collect samples from the foams prior this analysis, ATR-FTIR was the first characterization technique to be carried out on the foams before the CO_2 exposure and the last one to be performed after the treatment.

V.3.9 Micro Raman Spectroscopy (μ-Raman)

Raman spectra was obtained *in situ* and was carried out using a Horiba Jobin Yvon Labram 300 spectrometer (Stigmatic 300mm focal length spectrograph), equipped with a Olympus BX41 confocal microscope with high stability; He-Ne 17mW laser light-source operating at 632.8nm and a solid state laser at 532nm; a Peltier cooled CCD detector. The laser beam was focused with an Olympus 100x objective lens, with a spot size of 2 μm. The laser power at the surface of the samples was applied with no filters (full power); collection time was 25 seconds and 15 scans. Raman data analysis was performed using LabSpec 5 and OriginPro 8 software and all spectra were baseline-corrected.

V.3.10 CO_2 experiments

Supercritical CO_2 experiments in foam test samples were performed in the laboratory scale apparatus shown schematically in Figure V.3.1. Samples were introduced in a stainless-steel cell, with 33 mL of capacity and two sapphire windows to allow full visualisation of the samples during the process. Samples were firstly placed above a stainless-steel net and then into the cell (Figure V.3.2, A and B). For consolidation experiments, consolidants were introduced beneath the net, along with a magnetic stirring bar to promote dissolution (Figure V.3.2, C). The cell was immersed horizontally in a thermostatic water bath at 40 °C and the system was pressurized with fresh CO_2 until the desired pressure inside the cell was obtained (between 90 and 280 bar), using a Knauer blueshadow 40P liquid pump. For the continuous stream experiments, CO_2 was flowed through the vessel at a flow rate of 2 mL/min for the desired experimental time at constant p and T conditions (30 or 40 min).

The chosen experimental parameters for the first $scCO_2$ tests, in both discontinuous and continuous conditions, were based on the examples detailed in the Superwood patent [77], in which the temperature was gradually increased from 27 to 33°C at a maximum pressure of 100 bar within 30 minutes of experimental time at constant conditions. A $scCO_2$ continuous stream with water was also tested at the same conditions, in order to evaluate its safety for an eventual cleaning treatment and since one of the chosen consolidants was an aqueous dispersion. Based on the experiments performed by Sousa *et al.* [78, 79], the mass composition in this experiment was 99.75% CO_2 + 0.25% H_2O. Impregnation experiments with several consolidants (Section 3.1.2) were performed in discontinuous and isothermal conditions (40°C). Saturated supercritical streams were investigated at two different pressures, A (200 bar) and B (280 bar), with two hours of experimental time at constant p and T conditions. Decompression was performed manually, and its speed was slowly decreased throughout the experiments (from 120 to 5 minutes), to evaluate the foam samples resistance to the treatment and to avoid inducing damage to the material. Decompression time was increased to 10-25 minutes after the second consolidation experiment to minimize the observed expansion of the consolidants.

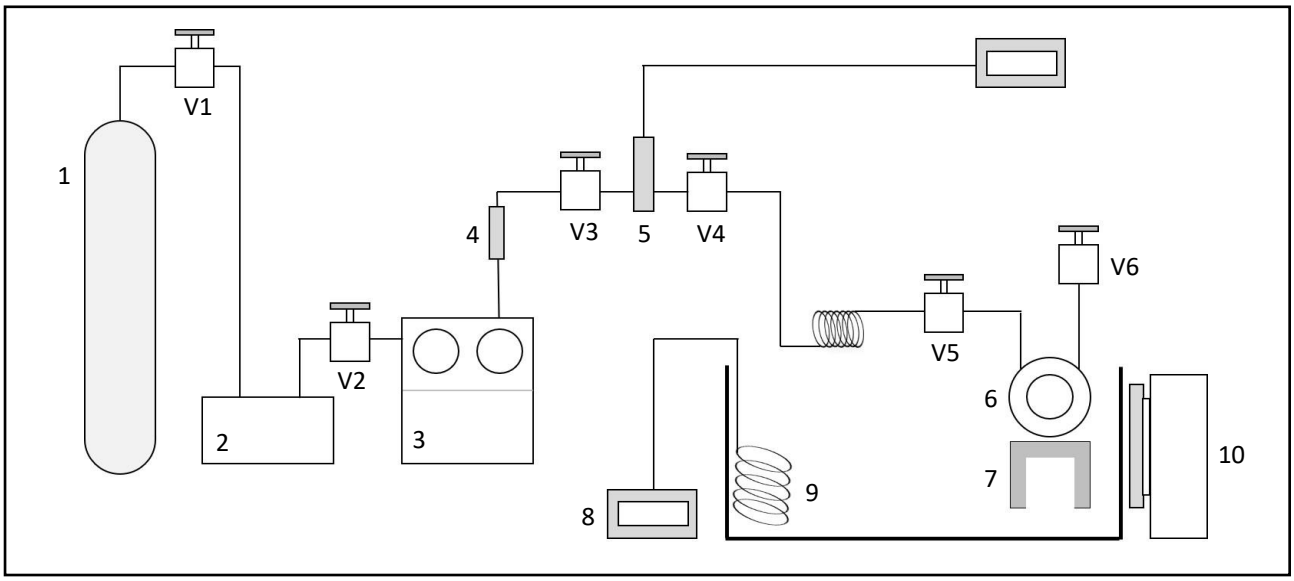


Figure V.3.1 – Schematic apparatus of the $scCO_2$ experiments: (1) CO_2 cylinder; (2) refrigerator unit; (3) high pressure pump; (4) check valve; (5) pressure transducer; (6) high pressure cell with sapphire windows; (7) cell supporter; (8) temperature controller; (9) thermostatic bath; (10) magnetic stirrer; (V1 to V6) pressure valves.

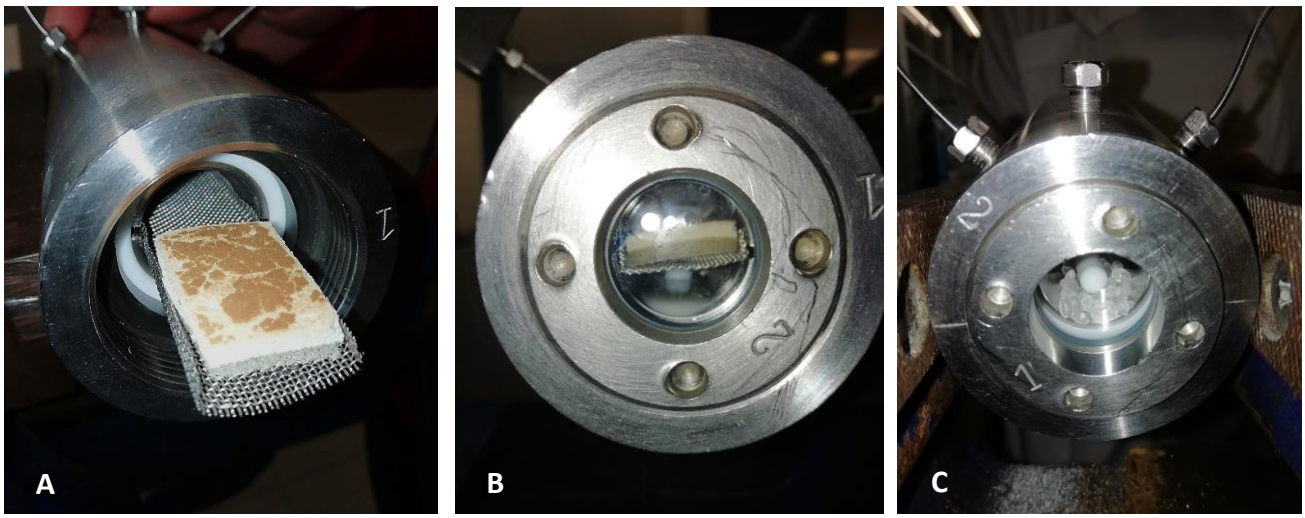
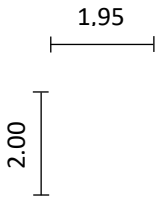
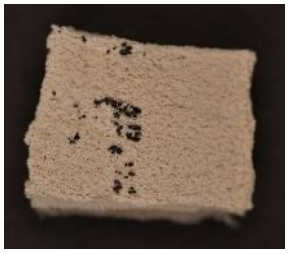
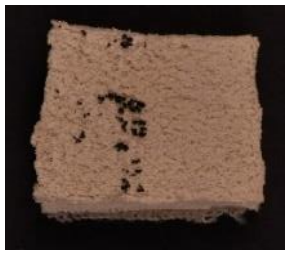
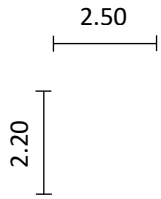
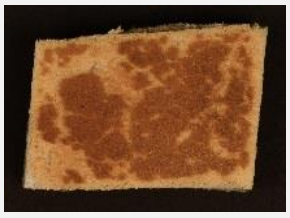
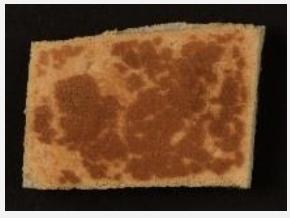
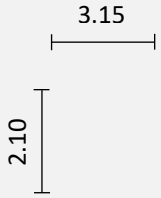
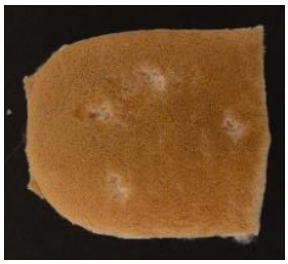
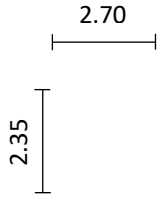
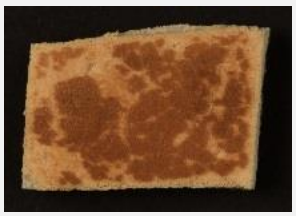
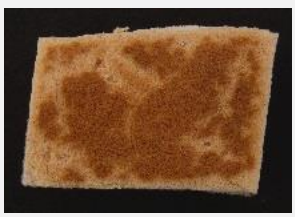
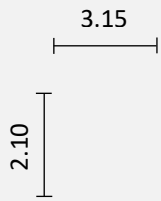


Figure V.3.2 – (A) Samples were introduced into the cell in a stainless-steel net. (B) The cell was equipped with two sapphire windows for full visualisation of the process. (C) Consolidants were introduced beneath the net with a magnetic stirring bar.

APPENDIX VI. Characterization of the samples pre and post-treatment

VI.1 Visual and dimensional analysis

Table VI.1.1 – Visual and dimensional variation of the treated samples, before and after the respective CO_2 experiment

Test	Sample	Visual		Dimension (cm)	
		Before	After	Before	After
1	K1NA				Unaltered
2	K1A				Unaltered
3	R1NA				Unaltered
4	N1A				Unaltered
5	K1A				Unaltered
6	N1A				Unaltered

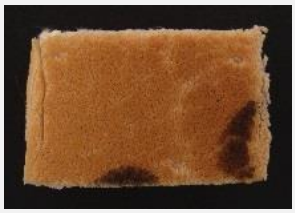
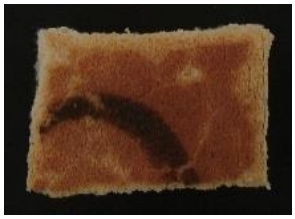
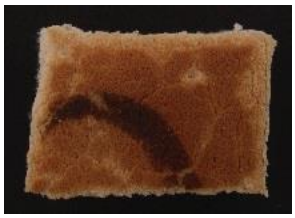
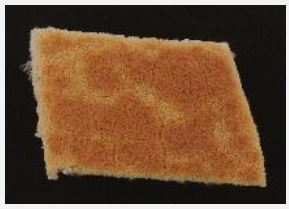
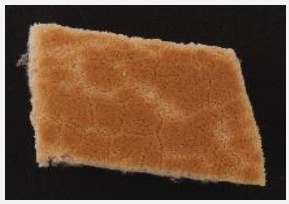
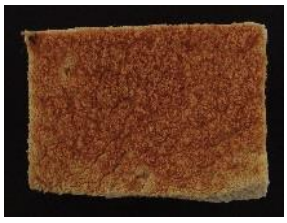
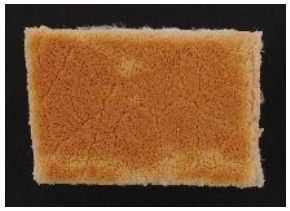
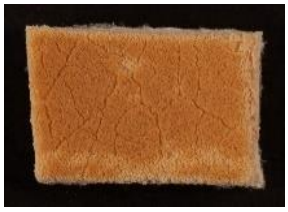
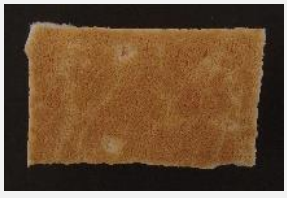
7	**R1A**			2.70 1.85	Unaltered
8	**K2A**			2.55 1.65	Unaltered
9	**K3A**			2.45 1.65	Unaltered
10	**N2A**			2.80 1.70	Unaltered
11	**R2A**			2.50 1.80	Unaltered
12	**K4A**			2.45 1.85	Unaltered
13	**N3A**			2.45 1.65 2.35 1.60	
14	**K5A**			2.45 1.50	Unaltered

Table VI.2.1 – Mass (g) measurements and variation of the treated samples, before and after the respective CO_2 experiment

Test		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Samples		K1NA	K1A	R1NA	N1A	K1A	N1A	R1A	K2A	K3A	N2A	R2A	K4A	N3A	K5A
Before	1	0.29362	0.47210	0.51965	0.37619	0.47192	0.37263	0.52064	0.30872	0.26334	0.25908	0.47503	0.29229	0.27446	0.25339
	2	0.29360	0.47220	0.51967	0.37615	0.47181	0.37262	0.52050	0.30873	0.26341	0.25910	0.47501	0.29232	0.27446	0.25333
	3	0.29365	0.47216	0.51969	0.37607	0.47174	0.37255	0.52040	0.30875	0.26346	0.25911	0.47503	0.29236	0.27448	0.25335
	A	0.29362	0.47215	0.51967	0.37614	0.47182	0.37260	0.52051	0.30873	0.26340	0.25910	0.47502	0.29232	0.27447	0.25336
	SD	0.00003	0.00005	0.00002	0.00006	0.00009	0.00004	0.00012	0.00002	0.00006	0.00002	0.00001	0.00004	0.00001	0.00003
After – First	1	0.29205	0.47009	0.51328	0.37203	0.46938	0.37167	0.54198	0.30606	0.26267	0.25506	0.46775	0.28919	0.27164	0.25330
	2	0.29216	0.47024	0.51347	0.37235	0.46938	0.37169	0.54204	0.30603	0.26262	0.25509	0.46779	0.28918	0.27165	0.25324
	3	0.29223	0.47002	0.51356	0.37252	0.46939	0.37159	0.54201	0.30602	0.26261	0.25513	0.46778	0.28912	0.27164	0.25326
	A	0.29215	0.47012	0.51344	0.37230	0.46938	0.37165	0.54201	0.30604	0.26263	0.25509	0.46777	0.28916	0.27164	0.25327
	SD	0.00009	0.00011	0.00014	0.00025	0.00001	0.00005	0.00003	0.00002	0.00003	0.00004	0.00002	0.00004	0.00001	0.00003
	% Δ	-0.14767	-0.20367	-0.62333	-0.38367	-0.24400	-0.09500	2.14967	-0.26967	-0.07700	-0.40033	-0.72500	-0.31600	-0.28233	-0.00900
After – Second	1	0.29232	0.47125	0.51496	0.37305	0.47287	0.36907	0.54236	0.30604	0.26131	0.25556	0.46939	0.28864	0.27178	0.25306
	2	0.29239	0.47123	0.51501	0.37308	0.47285	0.36902	0.54233	0.30603	0.2613	0.25555	0.46932	0.28863	0.27176	0.25311
	3	0.29237	0.47116	0.51503	0.37314	0.47284	0.36904	0.54232	0.30602	0.26129	0.25553	0.46929	0.28860	0.27175	0.25309
	A	0.29236	0.47121	0.51500	0.37309	0.47285	0.36904	0.54234	0.30603	0.26130	0.25555	0.46933	0.28862	0.27176	0.25309
	SD	0.00004	0.00005	0.00004	0.00005	0.00002	0.00003	0.00002	0.00001	0.00001	0.00002	0.00005	0.00002	0.00002	0.00003
	% Δ	-0.12633	-0.09400	-0.46700	-0.30467	0.10300	-0.35567	2.18233	-0.27033	-0.21033	-0.35500	-0.56900	-0.37000	-0.27033	-0.02700

A – average; SD – standard deviation

Table VI.3.1 – Colourimetry measurements and variation in two areas (A and B) for each treated sample, before and after the respective CO_2 experiment *(part I)*

Test			1			2			3			4			5			6			7		
Samples			K1NA			K1A			R1NA			N1A			K1A			N1A			R1A		
Coordinates			*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**
A	Before	1	73.41	1.55	17.78	61.37	10.91	39.47	73.12	0.77	11.91	65.39	15.89	45.31	62.45	10.40	39.09	66.21	15.17	46.74	61.51	9.87	38.20
		2	73.51	1.37	17.40	61.46	10.97	39.65	73.16	0.76	11.88	65.84	15.81	45.63	62.53	10.25	39.35	66.41	14.99	46.63	61.85	9.59	37.94
		3	73.31	1.49	17.74	61.58	11.00	39.74	71.88	0.75	11.46	65.37	15.97	45.34	62.58	10.39	39.45	66.58	14.91	46.64	60.97	10.11	38.23
		A	73.41	1.47	17.64	61.47	10.96	39.62	72.72	0.76	11.75	65.53	15.89	45.43	62.52	10.35	39.30	66.40	15.02	46.67	61.44	9.86	38.12
		SD	0.10	0.09	0.21	0.11	0.05	0.14	0.73	0.01	0.25	0.27	0.08	0.18	0.07	0.08	0.19	0.19	0.13	0.06	0.44	0.26	0.16
	After	1	72.86	1.06	18.81	62.45	10.40	39.09	71.01	0.83	11.74	66.21	15.17	46.74	63.21	10.35	39.85	67.35	13.14	43.24	61.76	8.99	37.75
		2	72.64	1.04	18.50	62.5z3	10.25	39.35	72.05	0.75	11.76	66.41	14.99	46.63	62.83	10.34	39.83	66.91	12.32	42.10	60.60	9.77	38.04
		3	72.77	0.99	18.08	62.58	10.39	39.45	72.78	0.8	12.13	66.58	14.91	46.64	64.83	10.02	38.94	66.88	12.81	42.61	61.22	9.33	37.90
		A	72.76	1.03	18.46	62.52	10.35	39.30	71.95	0.79	11.88	66.40	15.02	46.67	63.62	10.24	39.54	67.05	12.76	42.65	61.19	9.36	37.90
		SD	0.11	0.04	0.37	0.07	0.08	0.19	0.89	0.04	0.22	0.19	0.13	0.06	1.06	0.19	0.52	0.26	0.41	0.57	0.58	0.39	0.15
		Δ	-0.65	-0.44	0.82	1.05	-0.61	-0.32	-0.77	0.03	0.13	0.87	-0.87	1.24	1.10	-0.11	0.24	0.65	-2.27	-4.02	-0.25	-0.49	-0.23
	ΔE*			1.14			1.26			0.78			1.75			1.14			4.66			0.60	
B	Before	1	75.35	0.95	18.07	60.56	12.72	40.28	74.23	1.09	17.98	54.11	16.06	38.40	61.92	13.14	41.75	55.63	16.25	40.21	53.96	15.06	40.21
		2	74.35	1.01	17.81	60.21	12.33	39.80	74.16	1.07	18.01	56.03	15.70	39.13	61.63	12.76	41.25	56.04	15.88	39.49	55.09	14.39	40.28
		3	74.45	1.03	17.95	61.44	13.18	41.27	74.12	1.17	18.98	54.71	16.08	38.71	61.25	13.33	41.38	55.58	15.93	39.31	54.40	14.95	40.35
		A	74.72	1.00	17.94	60.74	12.74	40.45	74.17	1.11	18.32	54.95	15.95	38.75	61.60	13.08	41.46	55.75	16.02	39.67	54.48	14.80	40.28
		SD	0.55	0.04	0.13	0.63	0.43	0.75	0.06	0.05	0.57	0.98	0.21	0.37	0.34	0.29	0.26	0.25	0.20	0.48	0.57	0.36	0.07
	After	1	75.08	0.90	19.16	61.92	13.14	41.75	73.87	1.02	18.36	55.63	16.25	40.21	61.37	12.75	41.20	56.62	13.97	37.58	55.55	13.38	39.11
		2	75.19	0.81	19.07	61.63	12.76	41.25	73.56	0.96	19.17	56.04	15.88	39.49	61.34	12.65	41.11	55.96	14.31	37.48	55.82	13.23	39.17
		3	74.59	0.88	18.91	61.25	13.33	41.38	73.52	1.06	18.28	55.58	15.93	39.31	61.25	12.60	40.98	58.69	13.63	38.30	55.84	13.27	39.21
		A	74.95	0.86	19.05	61.60	13.08	41.46	73.65	1.01	18.60	55.75	16.02	39.67	61.32	12.67	41.10	57.09	13.97	37.79	55.74	13.29	39.16
		SD	0.32	0.05	0.13	0.34	0.29	0.26	0.19	0.05	0.49	0.25	0.20	0.48	0.06	0.08	0.11	1.42	0.34	0.45	0.16	0.08	0.05
		Δ	0.24	-0.13	1.10	0.86	0.33	1.01	-0.52	-0.10	0.28	0.80	0.07	0.92	-0.28	-0.41	-0.36	1.34	-2.05	-1.88	1.25	-1.51	-1.12
	ΔE*			1.14			1.37			0.60			1.22			0.62			3.09			2.26	

A – average; SD – standard deviation

Table VI.3.2 – Colourimetry measurements and variation in two areas (A and B) for each treated sample, before and after the respective CO_2 experiment (*part II*)

Test			8			9			10			11			12			13			14		
Samples			K2A			K3A			N2A			R2A			K4A			N3A			K5A		
Coordinates			*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**
A	Before	1	64.36	16.24	45.49	43.56	9.99	24.81	64.73	16.47	44.93	54.11	14.92	39.45	59.57	12.00	38.82	60.24	17.85	41.76	60.89	14.61	42.12
		2	65.01	16.03	45.76	45.90	10.46	27.03	63.71	17.03	44.59	54.08	14.77	39.41	58.64	12.46	38.66	60.06	17.84	41.68	60.73	14.87	42.25
		3	64.93	16.03	45.68	45.31	10.86	26.96	62.82	17.49	44.23	54.20	15.08	39.93	58.80	12.53	38.88	59.95	17.83	41.70	61.78	14.28	42.56
		A	64.77	16.10	45.64	44.92	10.44	26.27	63.75	17.00	44.58	54.13	14.92	39.60	59.00	12.33	38.79	60.08	17.84	41.71	61.13	14.59	42.31
		SD	0.35	0.12	0.14	1.22	0.44	1.26	0.96	0.51	0.35	0.06	0.16	0.29	0.50	0.29	0.11	0.15	0.01	0.04	0.57	0.30	0.23
	After	1	64.82	16.07	45.95	45.28	10.18	25.85	62.20	17.36	43.80	53.06	15.15	39.03	59.12	11.63	37.64	64.00	14.21	38.88	63.30	12.27	40.48
		2	65.32	15.92	46.24	45.70	10.22	26.13	63.91	16.44	44.27	52.99	15.13	38.85	59.46	11.43	37.70	64.72	14.14	39.73	63.48	12.33	40.41
		3	65.83	15.88	46.50	48.01	11.19	28.75	62.63	17.16	43.87	53.01	15.21	39.00	59.52	11.44	37.76	64.33	14.20	39.35	63.64	12.30	40.45
		A	65.32	15.96	46.23	46.33	10.53	26.91	62.91	16.99	43.98	53.02	15.16	38.96	59.37	11.50	37.70	64.35	14.18	39.32	63.47	12.30	40.45
		SD	0.51	0.10	0.28	1.47	0.57	1.60	0.89	0.48	0.25	0.04	0.04	0.10	0.22	0.11	0.06	0.36	0.04	0.43	0.17	0.03	0.04
		Δ	0.56	-0.14	0.59	1.41	0.09	0.64	-0.84	-0.01	-0.60	-1.11	0.24	-0.64	0.36	-0.83	-1.09	4.27	-3.66	-2.39	2.34	-2.29	-1.86
	ΔE*			0.82			1.55			1.03			1.30			1.41			6.11			3.77	
B	Before	1	57.99	17.66	42.06	51.92	16.89	37.53	63.40	17.79	45.07	53.94	14.92	40.30	58.12	11.63	37.56	62.67	17.94	44.11	59.04	14.50	41.44
		2	59.18	17.48	42.78	51.87	16.87	37.39	63.35	17.75	44.95	53.98	15.08	40.42	59.18	11.50	37.92	62.91	17.86	44.14	57.77	14.44	40.56
		3	58.14	18.19	42.81	51.73	16.90	37.33	63.19	17.94	44.94	54.11	15.00	40.54	58.51	11.66	37.72	63.05	17.80	44.42	57.90	14.54	40.77
		A	58.44	17.78	42.55	51.84	16.89	37.42	63.31	17.83	44.99	54.01	15.00	40.42	58.60	11.60	37.73	62.88	17.87	44.22	58.24	14.49	40.92
		SD	0.65	0.37	0.42	0.10	0.02	0.10	0.11	0.10	0.07	0.09	0.08	0.12	0.54	0.09	0.18	0.19	0.07	0.17	0.70	0.05	0.46
	After	1	60.19	16.65	43.11	52.78	16.59	37.30	63.22	17.47	44.79	53.10	15.00	39.28	59.55	10.80	36.95	66.80	13.86	40.71	61.17	12.01	39.43
		2	59.79	15.69	43.06	52.91	16.65	37.50	63.41	17.26	44.78	53.20	14.93	39.30	59.20	10.98	37.05	67.31	13.69	40.84	62.03	11.82	39.62
		3	59.53	16.53	43.24	52.81	16.72	37.46	63.14	17.45	44.84	52.92	14.90	39.17	59.53	10.90	37.02	66.99	13.81	40.71	61.16	12.02	39.41
		A	59.84	16.29	43.14	52.83	16.65	37.42	63.26	17.39	44.80	53.07	14.94	39.25	59.43	10.89	37.01	67.03	13.79	40.75	61.45	11.95	39.49
		SD	0.33	0.52	0.09	0.07	0.07	0.11	0.14	0.12	0.03	0.14	0.05	0.07	0.20	0.09	0.05	0.26	0.09	0.08	0.50	0.11	0.12
		Δ	1.40	-1.49	0.59	0.99	-0.23	0.00	-0.06	-0.43	-0.18	-0.94	-0.06	-1.17	0.82	-0.70	-0.73	4.16	-4.08	-3.47	3.22	-2.54	-1.44
	ΔE*			2.12			1.02			0.47			1.50			1.30			6.78			4.35	

A – average; SD – standard deviation

VI.4 Infrared spectroscopy

VI.4.1 Foam samples

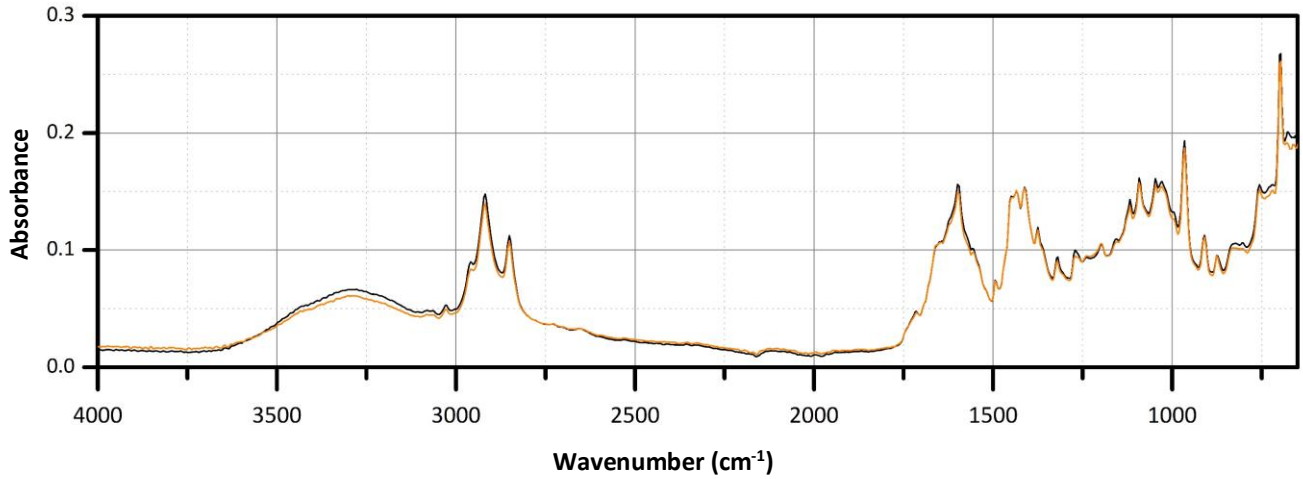


Figure VI.4.1 – Infrared spectra of sample K1NA before (black) and after (orange) $scCO_2$ treatment with discontinuous stream.

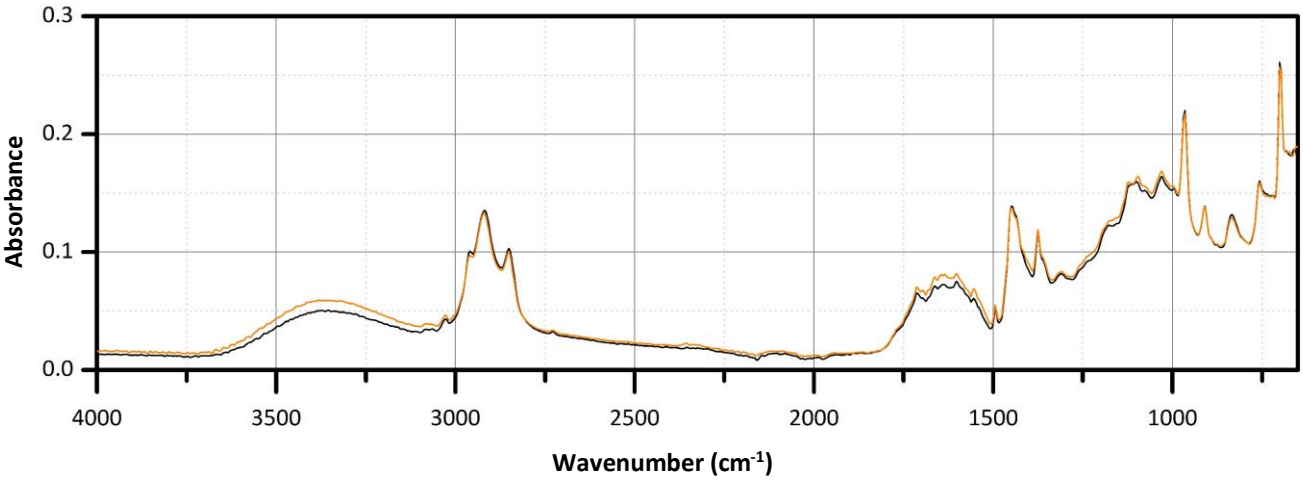


Figure VI.4.2 – Infrared spectra of sample K1A before (black) and after (orange) $scCO_2$ treatment with discontinuous stream.

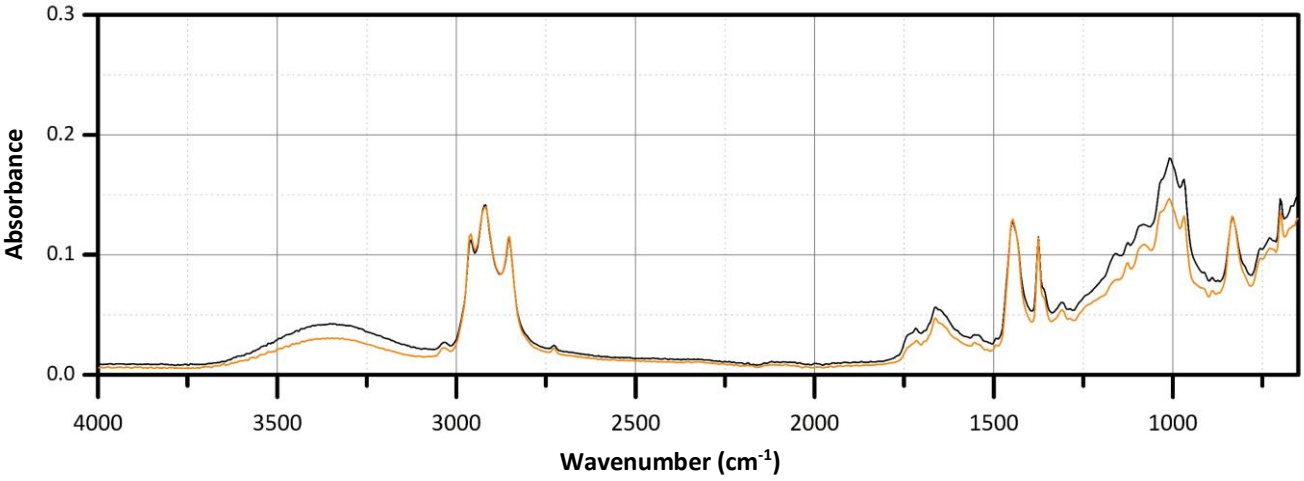


Figure VI.4.3 – Infrared spectra of sample R1NA before (black) and after (orange) $scCO_2$ treatment with continuous stream.

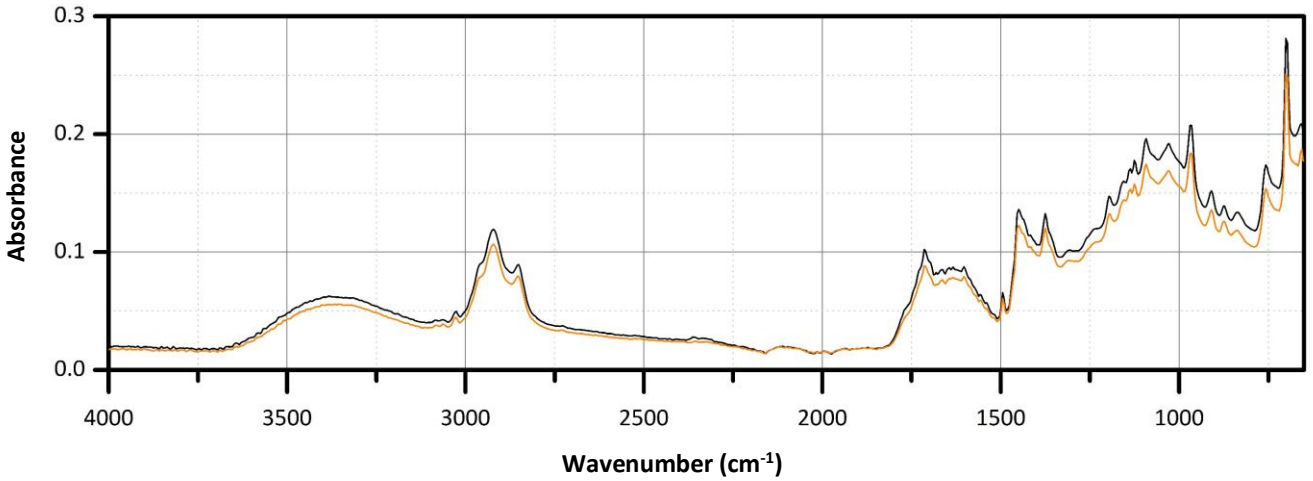


Figure VI.4.4 – Infrared spectra of sample N1A before (black) and after (orange) $scCO_2$ treatment with continuous stream.

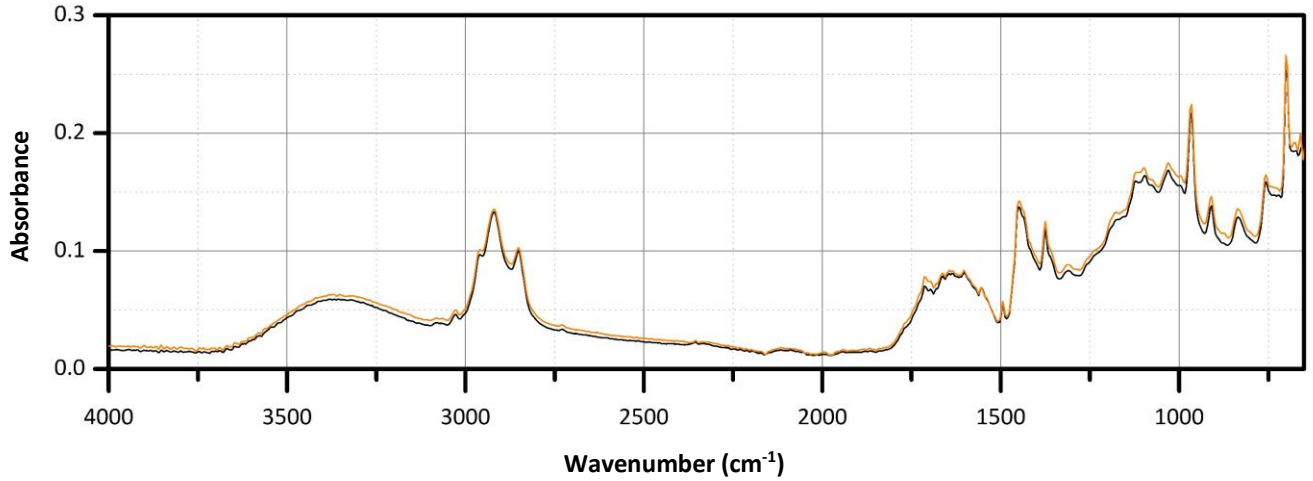


Figure VI.4.5 – Infrared spectra of sample K1A before (black) and after (orange) $scCO_2$ treatment with a co-solvent (H_2O).

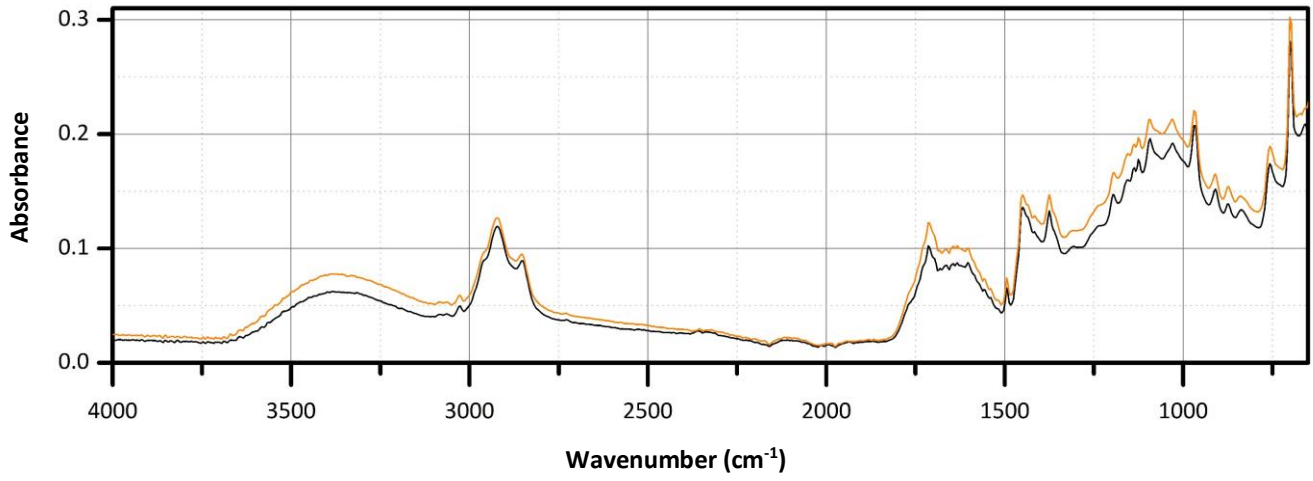


Figure VI.4.6 – Infrared spectra of sample N1A before (black) and after (orange) $scCO_2$ treatment with Evacon (25%, condition A).

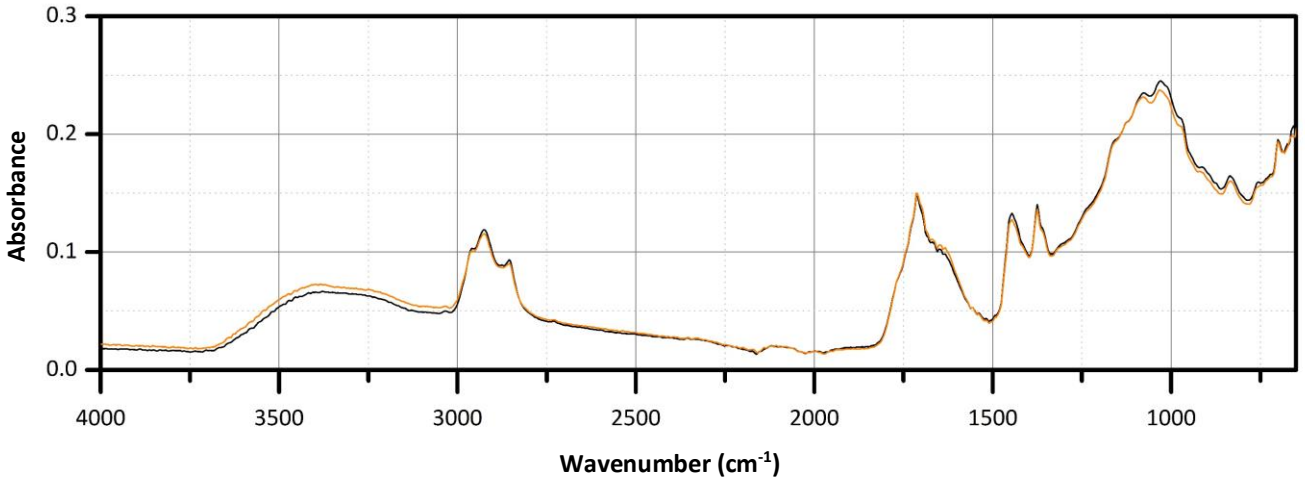


Figure VI.4.7 – Infrared spectra of sample R1A before (black) and after (orange) $scCO_2$ treatment with Evacon (100%, condition A).

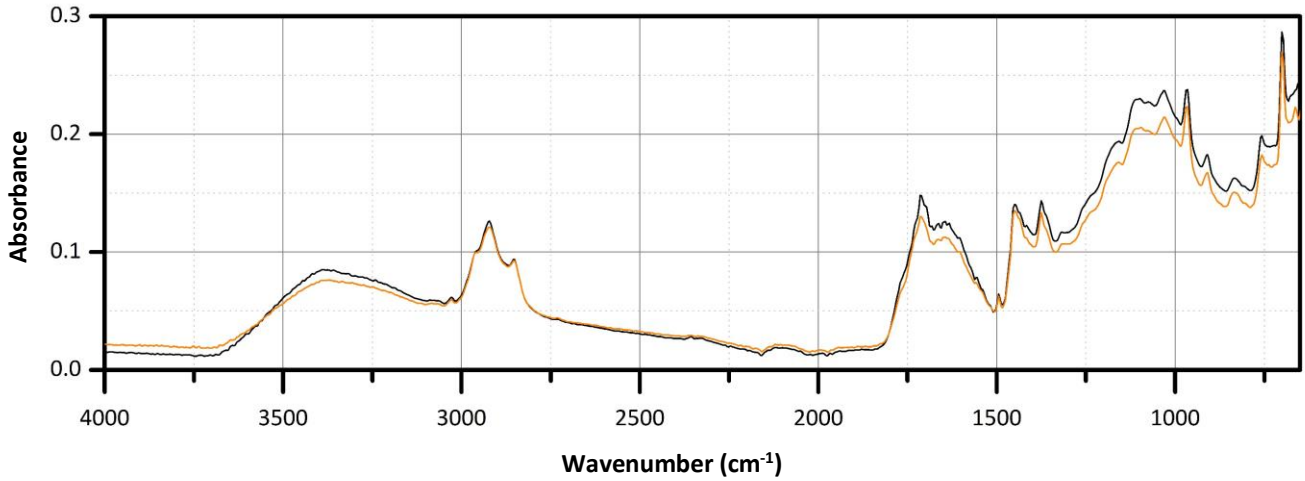


Figure VI.4.8 – Infrared spectra of sample K2A before (black) and after (orange) $scCO_2$ treatment with PB72 (condition A).

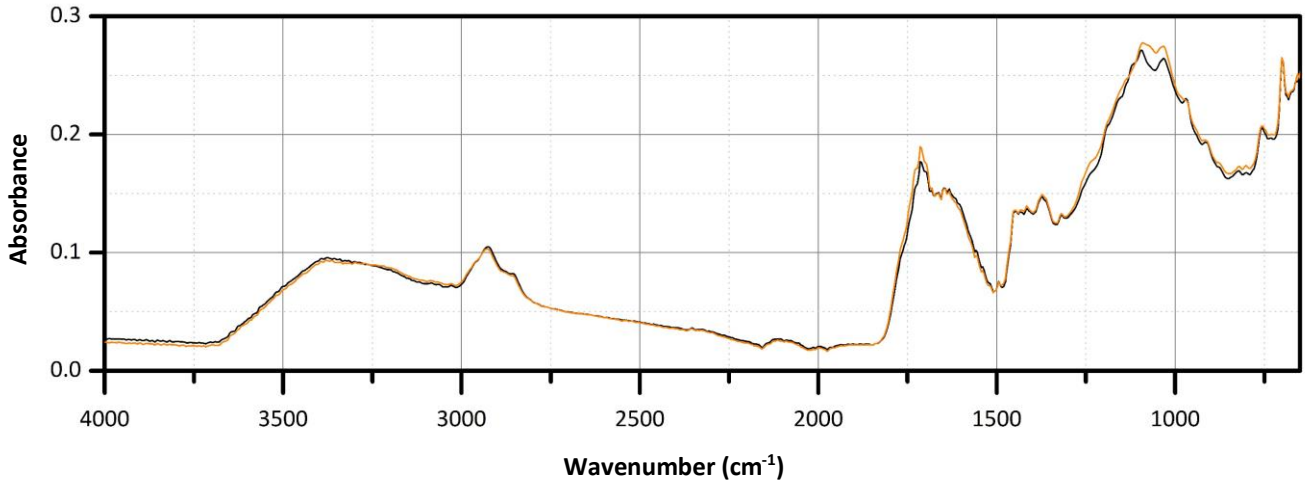


Figure VI.4.9 – Infrared spectra of sample K3A before (black) and after (orange) $scCO_2$ treatment with EVA (condition A).

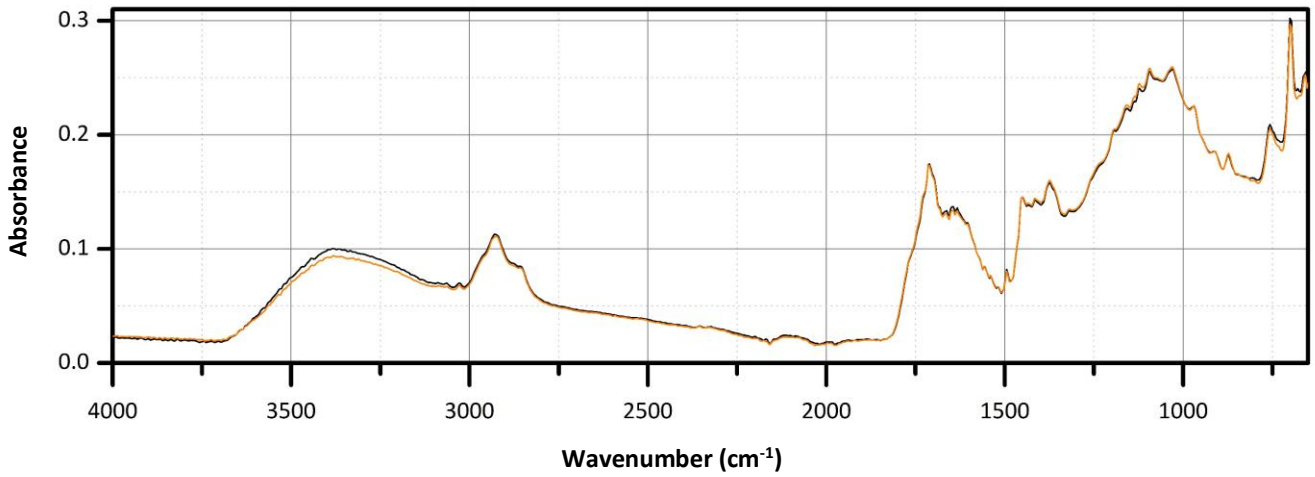


Figure VI.4.10 – Infrared spectra of sample N2A before (black) and after (orange) $scCO_2$ treatment with EVA (condition B).

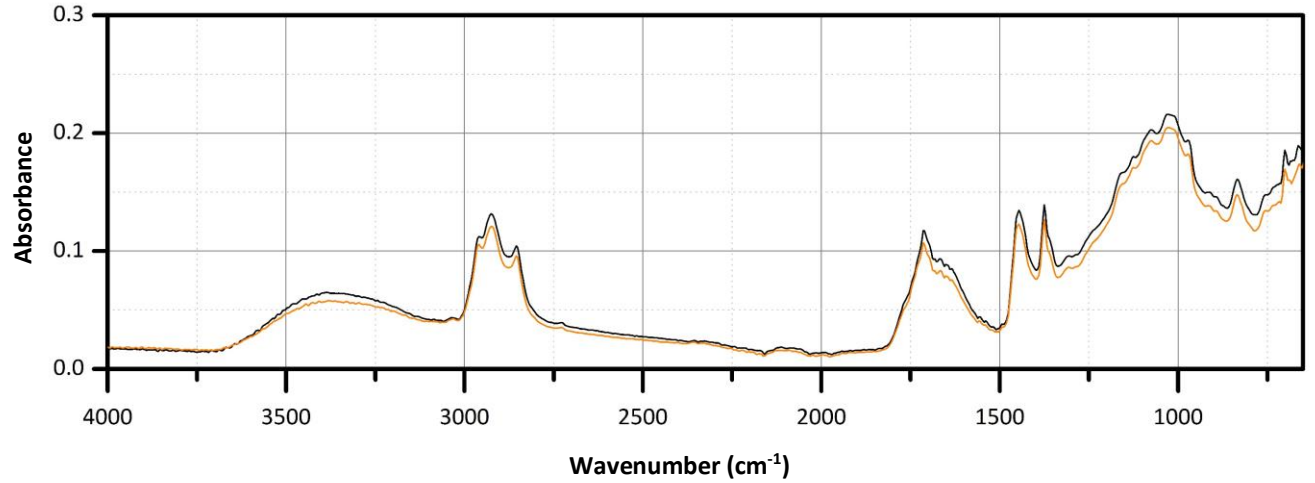


Figure VI.4.11 – Infrared spectra of sample R2A before (black) and after (orange) $scCO_2$ treatment with PB72 (condition B).

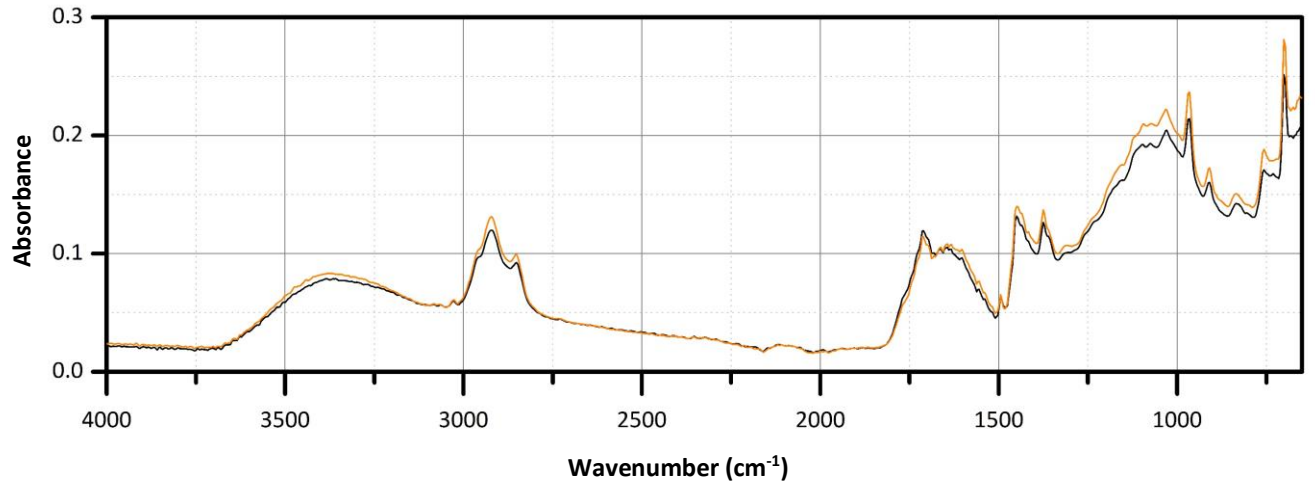


Figure VI.4.12 – Infrared spectra of sample K4A before (black) and after (orange) $scCO_2$ treatment with Evacon (100%, condition B).

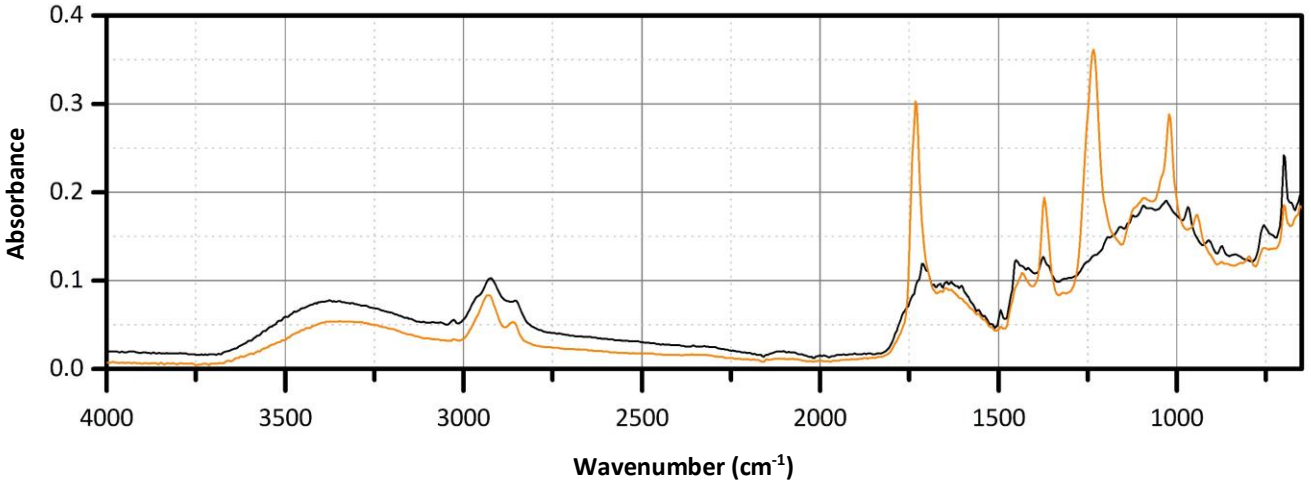


Figure VI.4.13 – Infrared spectra of sample N3A before (black) and after (orange) $scCO_2$ treatment with PVAc (condition B).

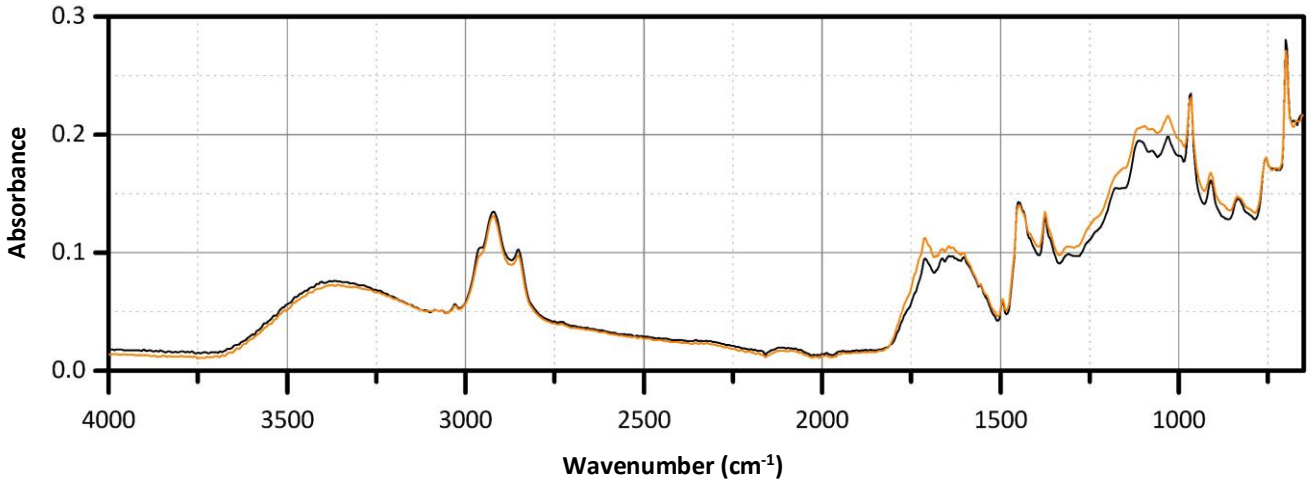


Figure VI.4.14 – Infrared spectra of sample K5A before (black) and after (orange) $scCO_2$ treatment with Regalrez (condition B).

Table VI.4.1 – Infrared assignment of the relevant bands of polyisoprene and poly(butadiene-styrene)

Polyisoprene [15]		**Poly(butadiene-styrene)** [17]	
Wavenumber (cm^{-1})	**Assignment**	**Wavenumber (cm^{-1})**	**Assignment**
3036 (w)	ν(=C-H)	3077	ν(C-H)
2962 (vs)	$\nu_{as}(CH_3)$	3025	ν(C-H)
2928 (vs)	$\nu_{as}(CH_2)$	2919	$\nu_{as}(CH_3)$
2855 (vs)	$\nu_s(CH_2)$	2845	$\nu_s(CH_3)$
1450 (w)	$\delta(CH_2)$	1493	ν(aromatic ring)
1377 (s)	$\delta_{as}(CH_3)$	1450	$\delta(CH_2)$
889 (mw)	$\delta(CH_3)$	967	δ(C-H) (1,4-*trans*)
837 (m)	δ(=C-H)	910	δ(C-H) (1,2 vinyl)
		758	δ(C-H) (phenyl groups)
		700	δ(C-H) (1,4-*cis*)

ν – stretching; δ – bending (scissoring); s – symmetric; as – asymmetric

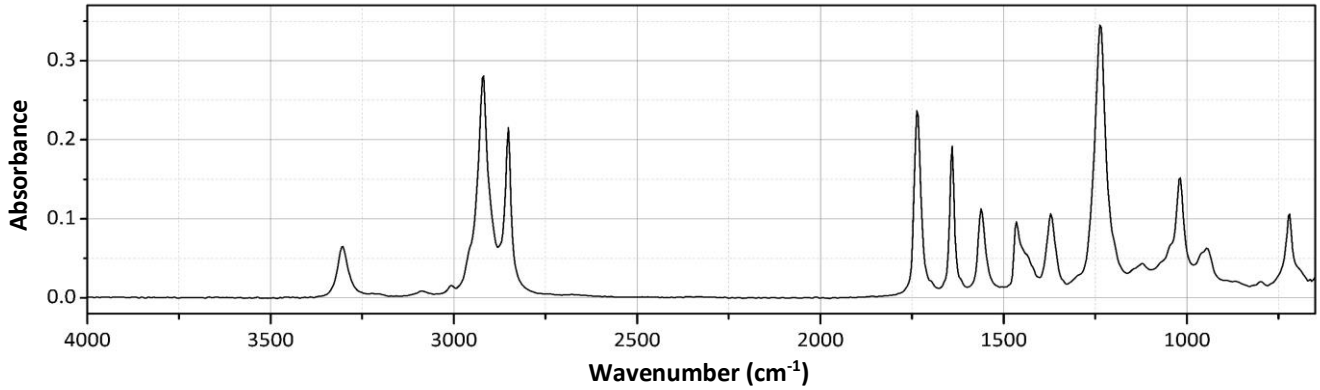


Figure VI.4.15 – Infrared spectra of the consolidant EVA.

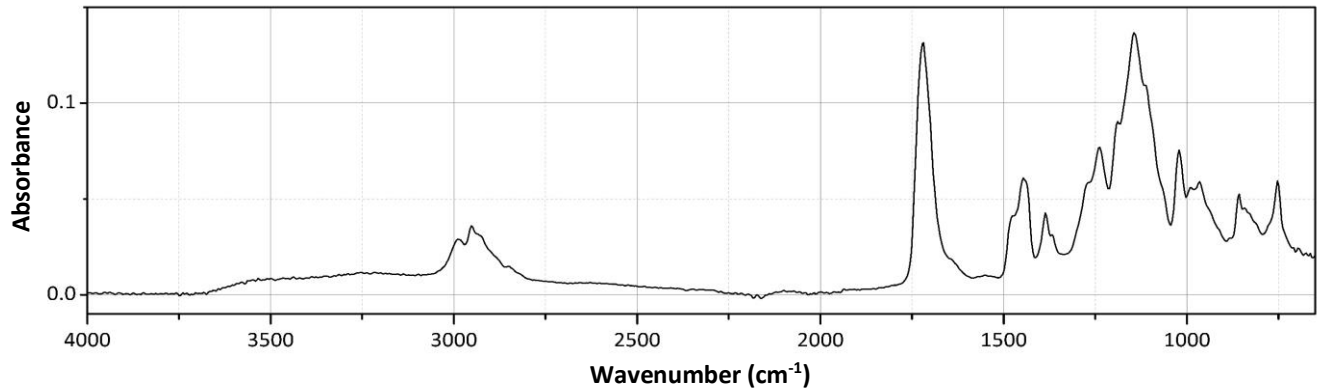


Figure VI.4.16 – Infrared spectra of the consolidant Paraloid™ B72.

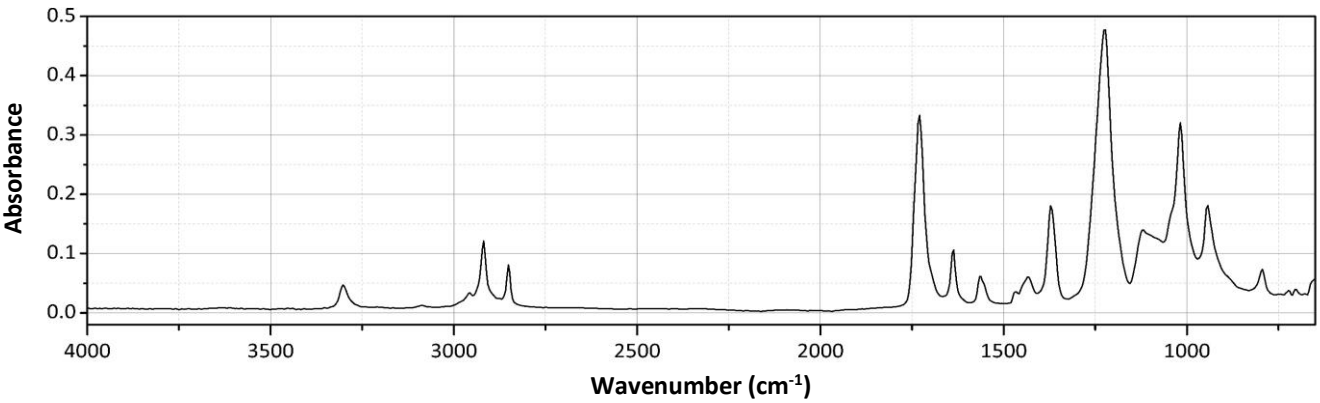


Figure VI.4.17 – Infrared spectra of the consolidant PVAc.

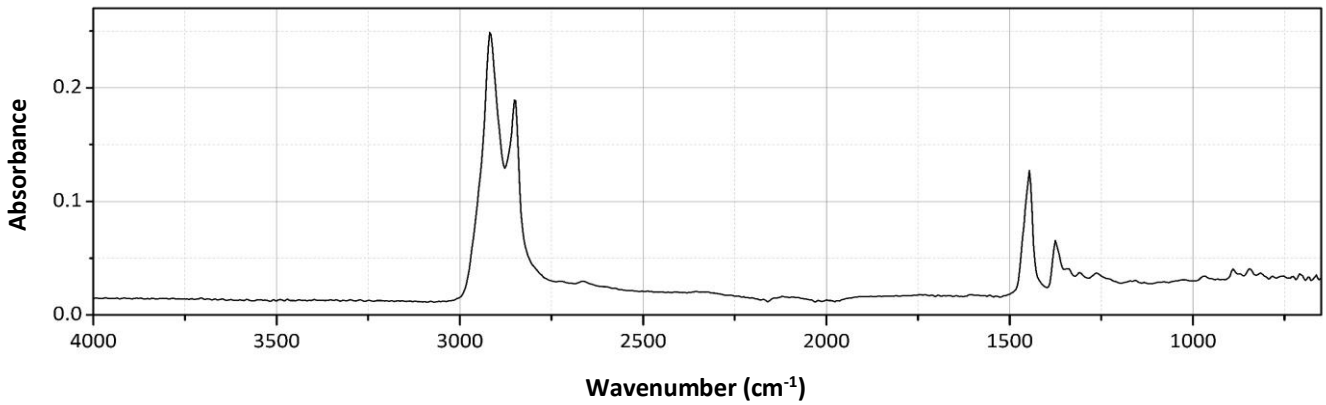


Figure VI.4.18 – Infrared spectra of the consolidant Regalrez™ 1094.

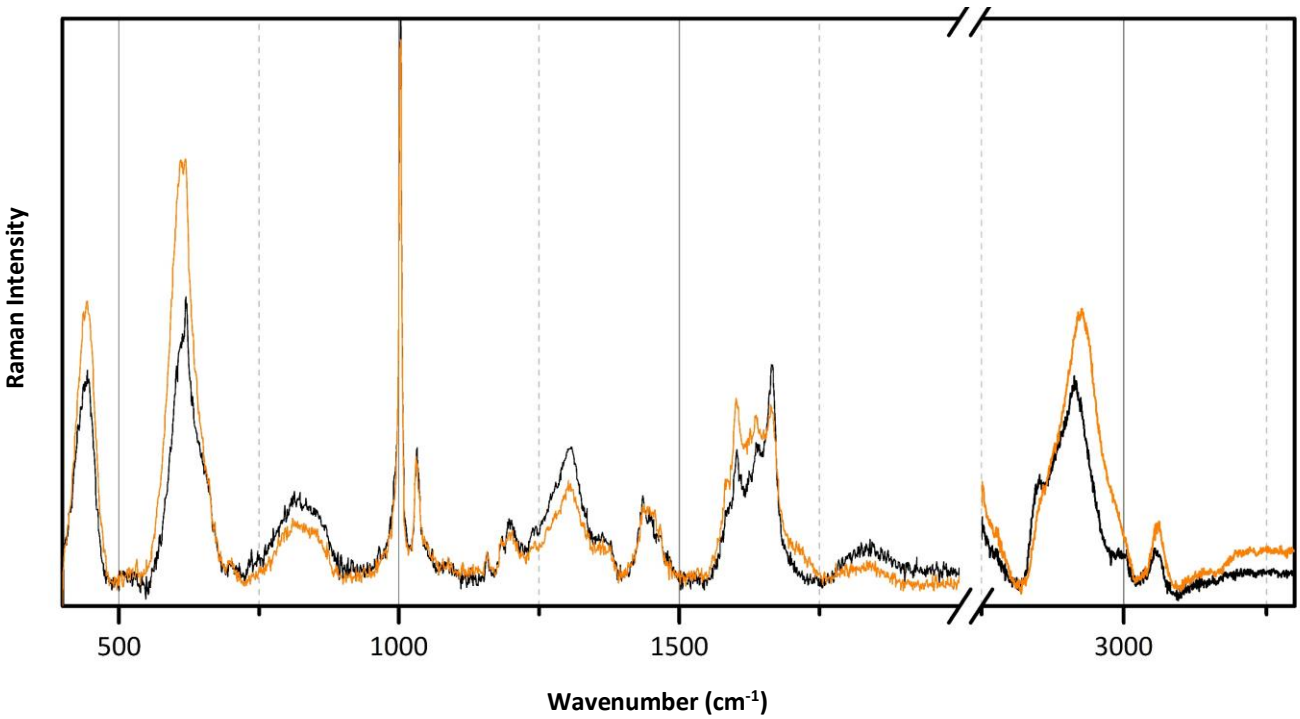


Figure VI.5.1 – Raman spectra of sample K1NA, before (black) and after (orange) $scCO_2$ treatment with discontinuous stream.

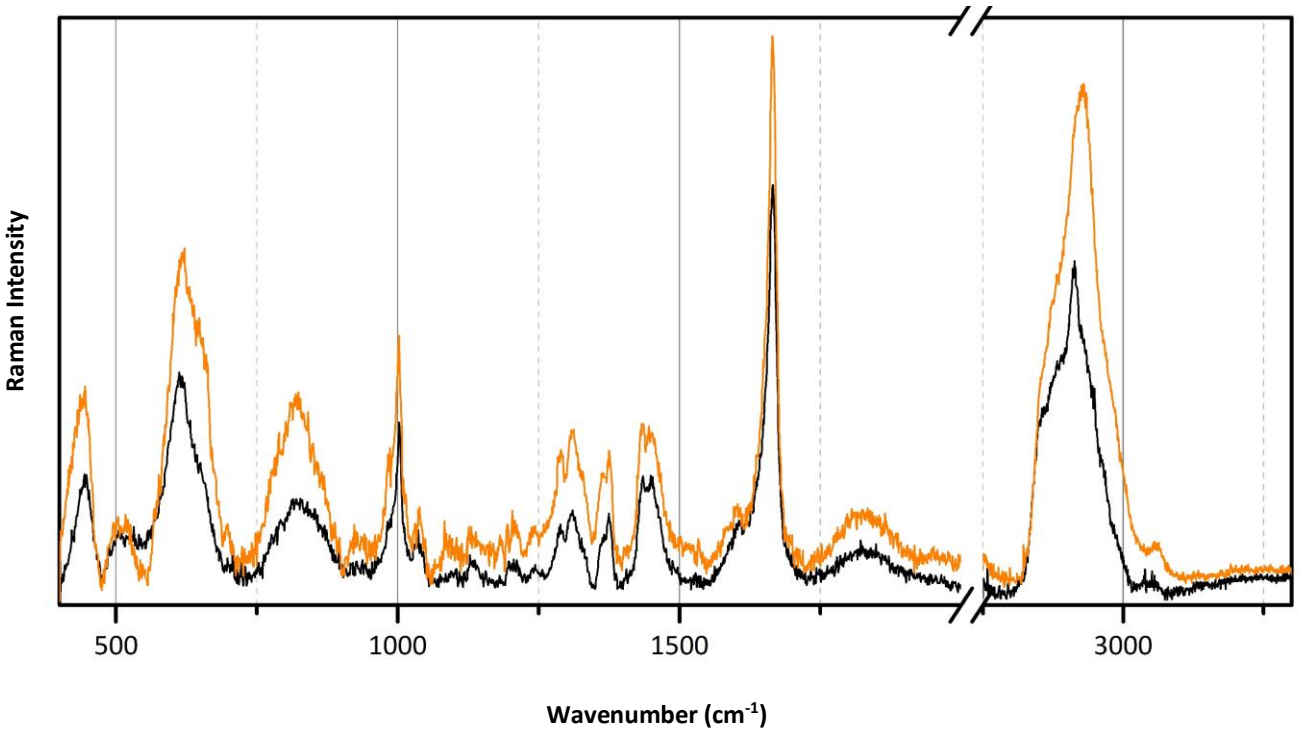


Figure VI.5.2 – Raman spectra of sample R1NA, before (black) and after (orange) $scCO_2$ treatment with continuous stream.

Table VI.5.1 – Raman assignment of the relevant bands of polyisoprene, polybutadiene and polystyrene

Wavenumber (cm^{-1})	Polymer	Assignment	Reference
2913	PI	$\nu_{as}(CH_2)$	[67, 68]
1664-1666	PI	ν(C=C) *1,4*	[67, 68]
1637	PI	ν(C=C) vinyl	[67]
	PB		[69]
1603-1605	PS	Ring skeletal ν(CC)	[70]
1446-1449	PI	$\delta_{as}(CH_3)$	[67]
1434-1435	PI	$\delta_s(CH_2)$	[67, 68]
	PB	$\delta(CH_2)$	[69]
1374	PI		[67, 68]
1304-1310	PB	δ(=CH)	[69]
1289	PI	δ (CH_2)	[68]
1200	PS	ν(C-C)	[70]
1128	PI	ν(C-C) *cis*	[67]
	PB	ν_{as}(C-C) *trans*	[69]
1032-1037	PS	ring δ(C-H)	[70]
1003	PB	ν_{as}(C-C)	[69]
	PS	Ring breathing mode	[70]
613-620	PS	ring δ	[70]

PI – polyisoprene; PB – polybutadiene; PS – polystyrene; ν – stretching; δ – bending; s – symmetric; as – asymmetric